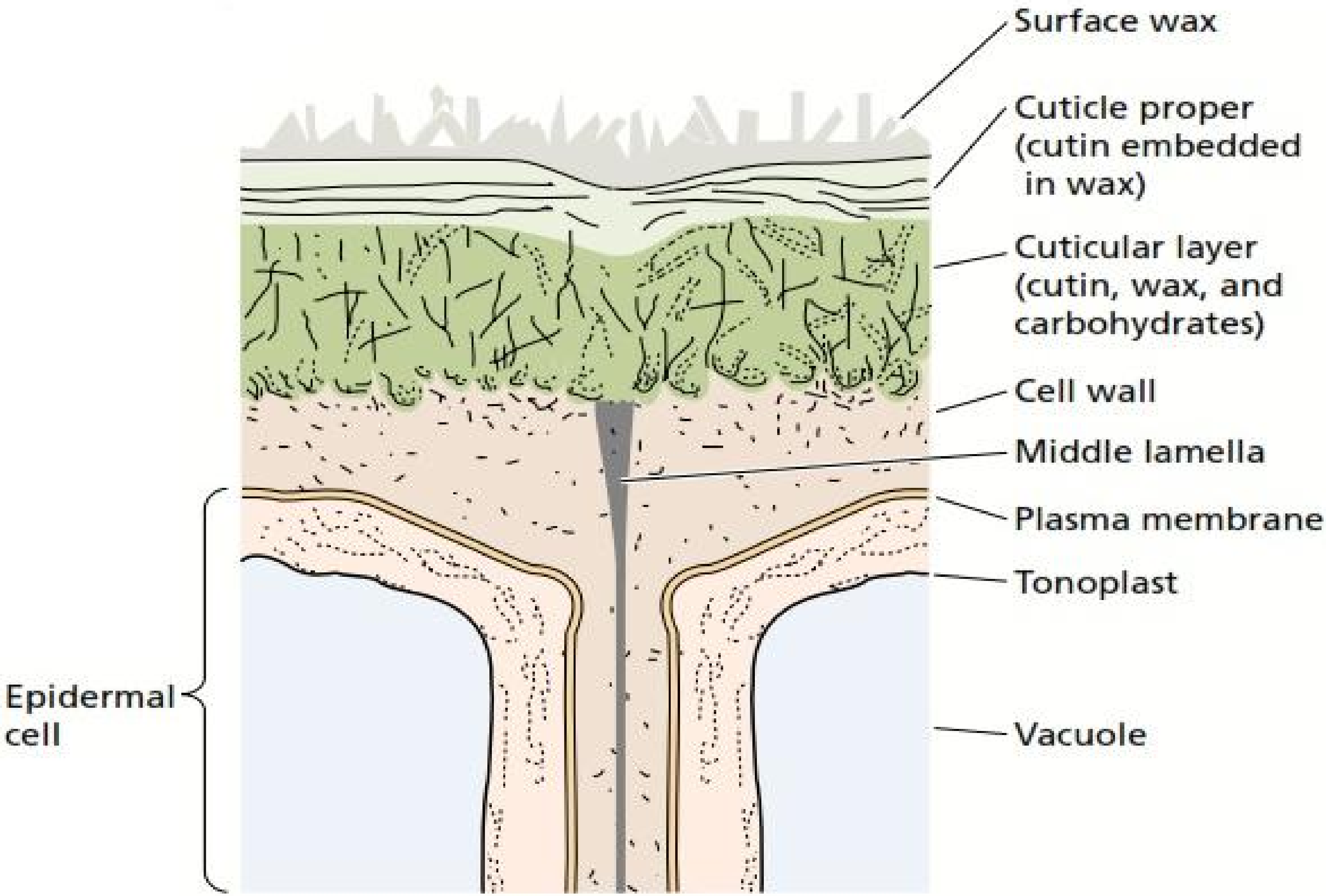
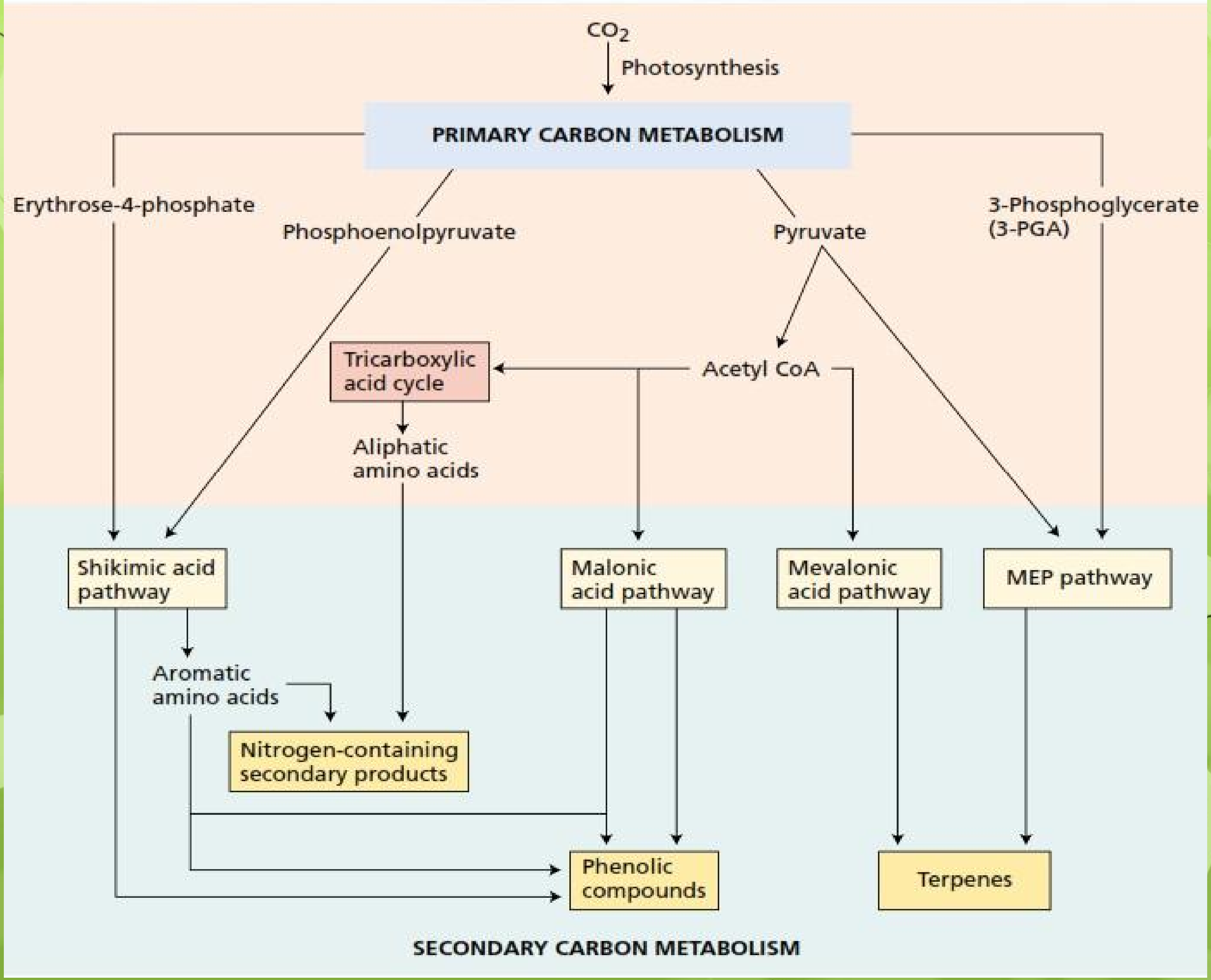
Secondary Metabolites and Biotic Stress

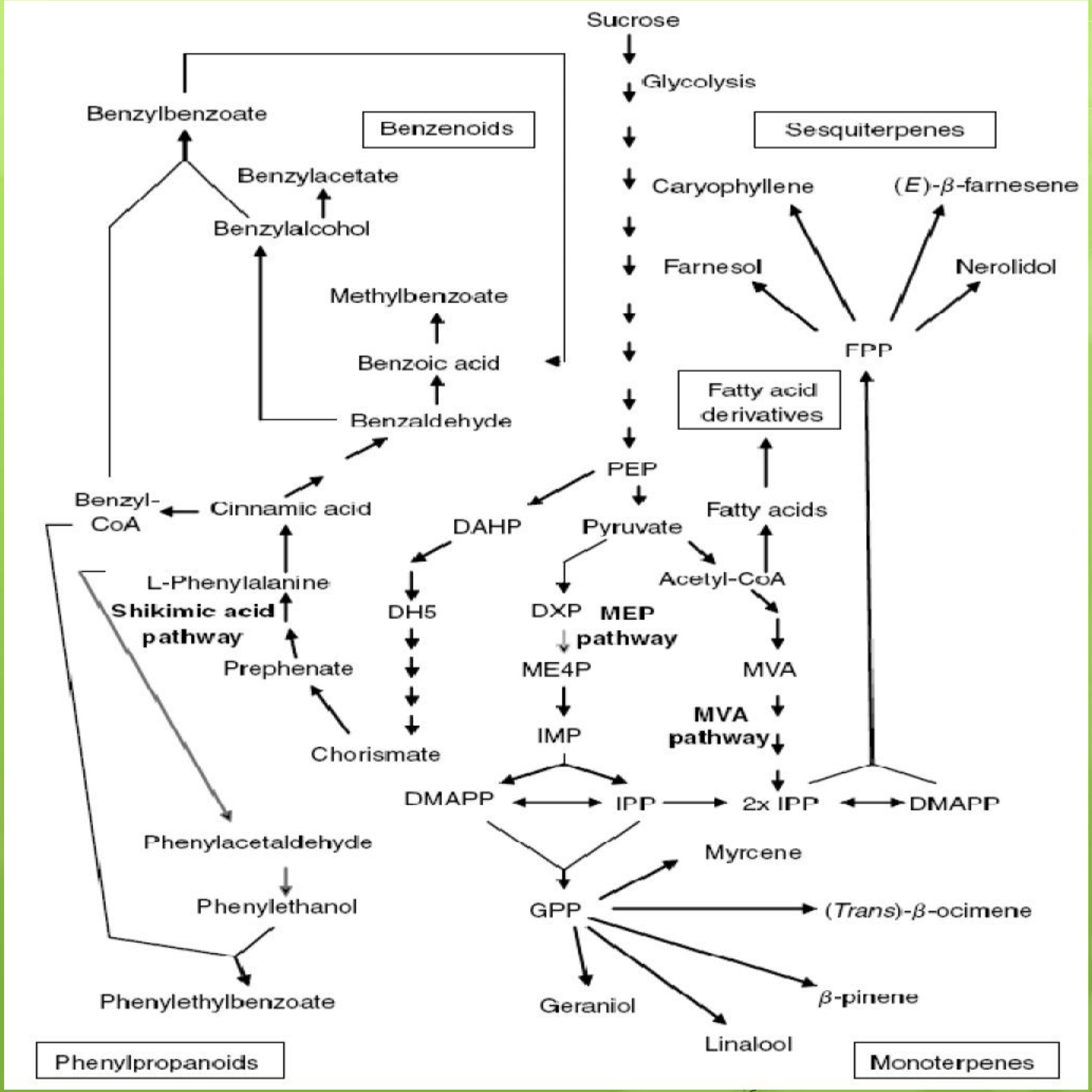

Surface wax
Cuticle proper (cutin embedded in wax)
Cuticular layer (cutin, wax, and carbohydrates)
Cell wall
Middle lamella
Plasma membrane
Tonoplast
Vacuole
Epidermal cell

Secondary Metabolites Major Groups

Plant secondary metabolites can be divided into three and/or four chemically distinct groups:

- **Terpenes**
- **Phenolics compounds**
- **Nitrogen-containing compounds**
- **Fatty acid compounds**

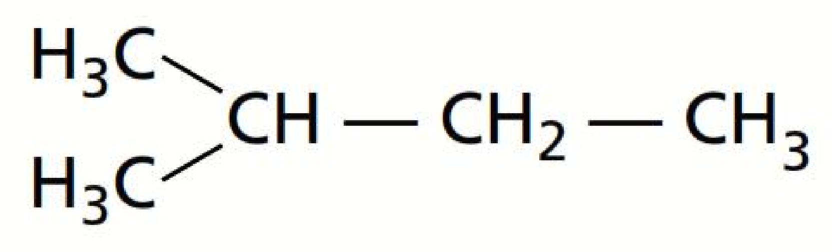

CO2
Photosynthesis
PRIMARY CARBON METABOLISM
Erythrose-4-phosphate
Phosphoenolpyruvate
Pyruvate
3-Phosphoglycerate (3-PGA)
Tricarboxylic acid cycle
Acetyl CoA
Aliphatic amino acids
Shikimic acid pathway
Malonic acid pathway
Mevalonic acid pathway
MEP pathway
Aromatic amino acids
Nitrogen-containing secondary products
Phenolic compounds
Terpenes
SECONDARY CARBON METABOLISM


Sucrose
Glycolysis
Benzylbenzoate
Benzenoids
Sesquiterpenes
Benzylacetate
Caryophyllene
(E)-β-farnesene
Benzylalcohol
Farnesol
Nerolidol
Methylbenzoate
FPP
Benzoic acid
Fatty acid derivatives
Benzaldehyde
PEP
Benzyl-CoA
Cinnamic acid
Fatty acids
DAHP
Pyruvate
L-Phenylalanine
Acetyl-CoA
Shikimic acid pathway
DH5
DXP
MEP pathway
Prephenate
ME4P
MVA
MVA pathway
IMP
Chorismate
DMAPP
IPP
2x IPP
DMAPP
Phenylacetaldehyde
Myrcene
Phenylethanol
GPP
(Trans)-β-ocimene
Phenylethylbenzoate
Geraniol
β-pinene
Linalool
Phenylpropanoids
Monoterpenes

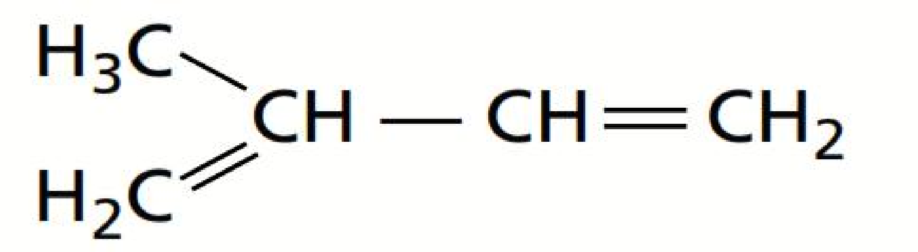
TERPENES

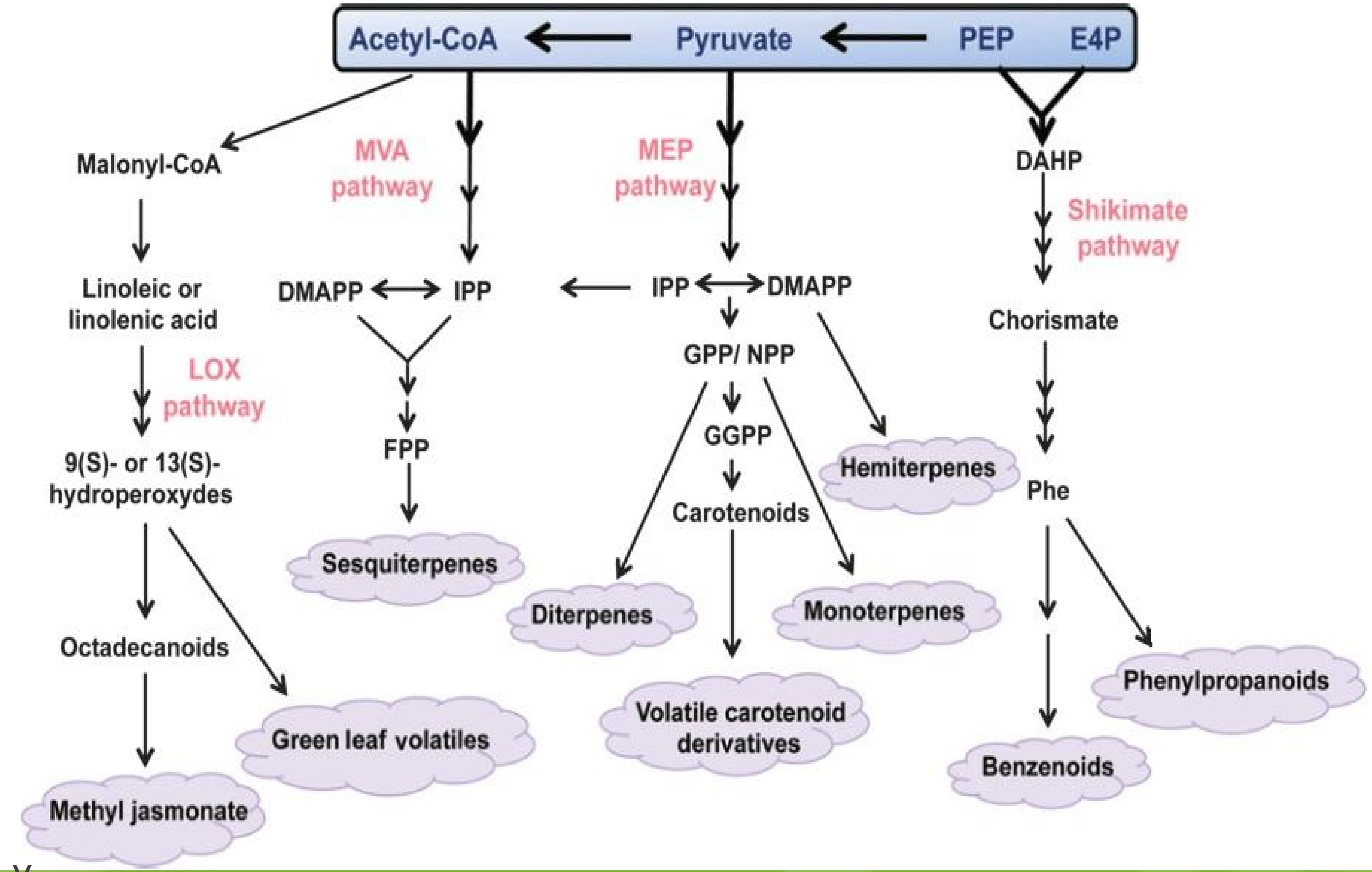
- **All terpenes are derived from the union of five-carbon elements that have the branched carbon skeleton of isopentane.**
- **The basic structural elements of terpenes are sometimes called isoprene units because terpenes can decompose at high temperatures to give isoprene.**
- *Thus all terpenes are occasionally referred to as* ***isoprenoids****.*

isopentane



isoprene units





Acetyl-CoA ← Pyruvate ← PEP E4P

Malonyl-CoA

Linoleic or linolenic acid

LOX pathway

9(S)- or 13(S)-hydroperoxydes

Octadecanoids

Methyl jasmonate

Green leaf volatiles

MVA pathway

DMAPP ↔ IPP

FPP

Sesquiterpenes

MEP pathway

IPP ↔ DMAPP

GPP/ NPP

GGPP

Carotenoids

Volatile carotenoid derivatives

Diterpenes

Monoterpenes

Hemiterpenes

DAHP

Shikimate pathway

Chorismate

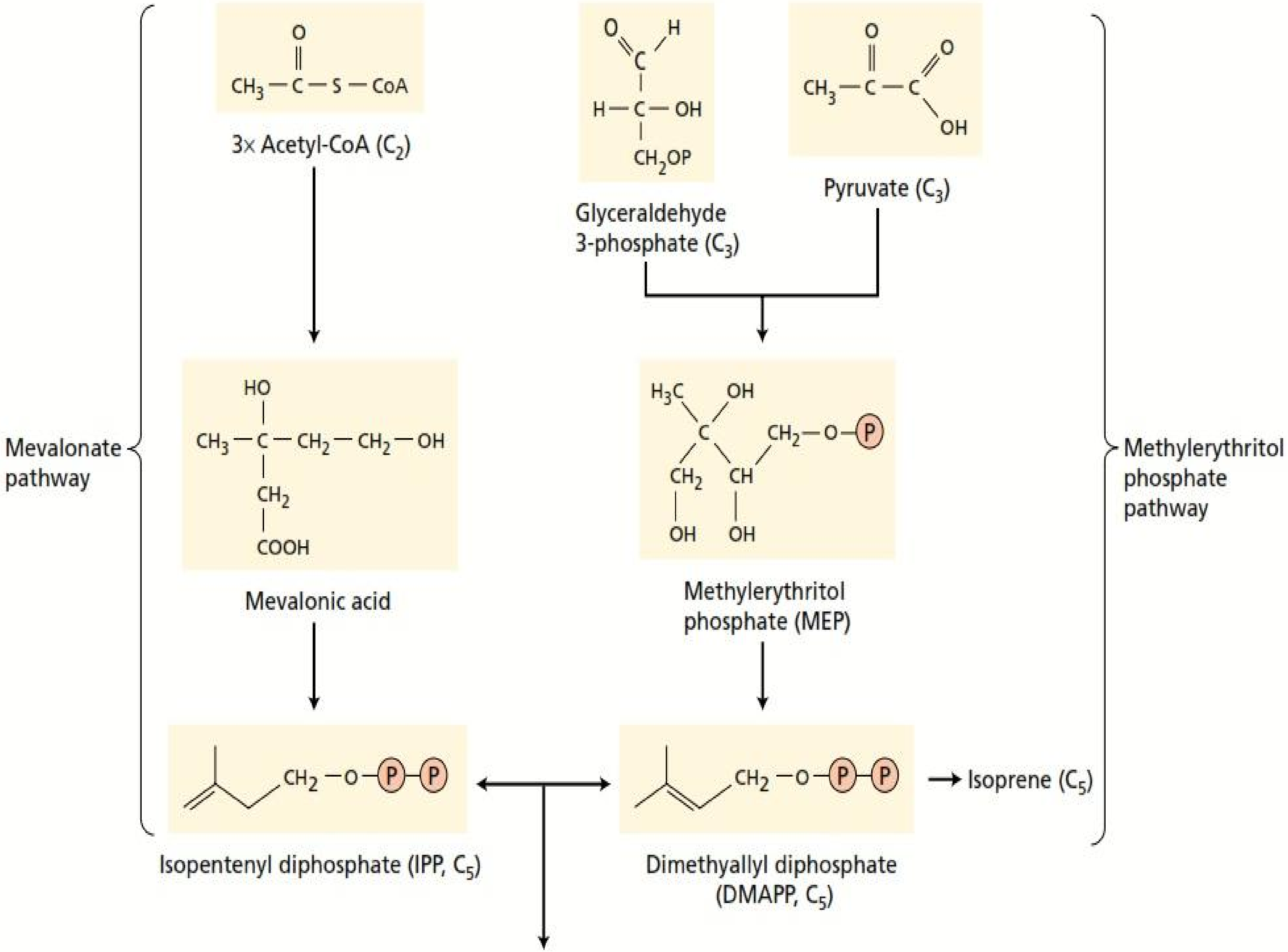
Phe

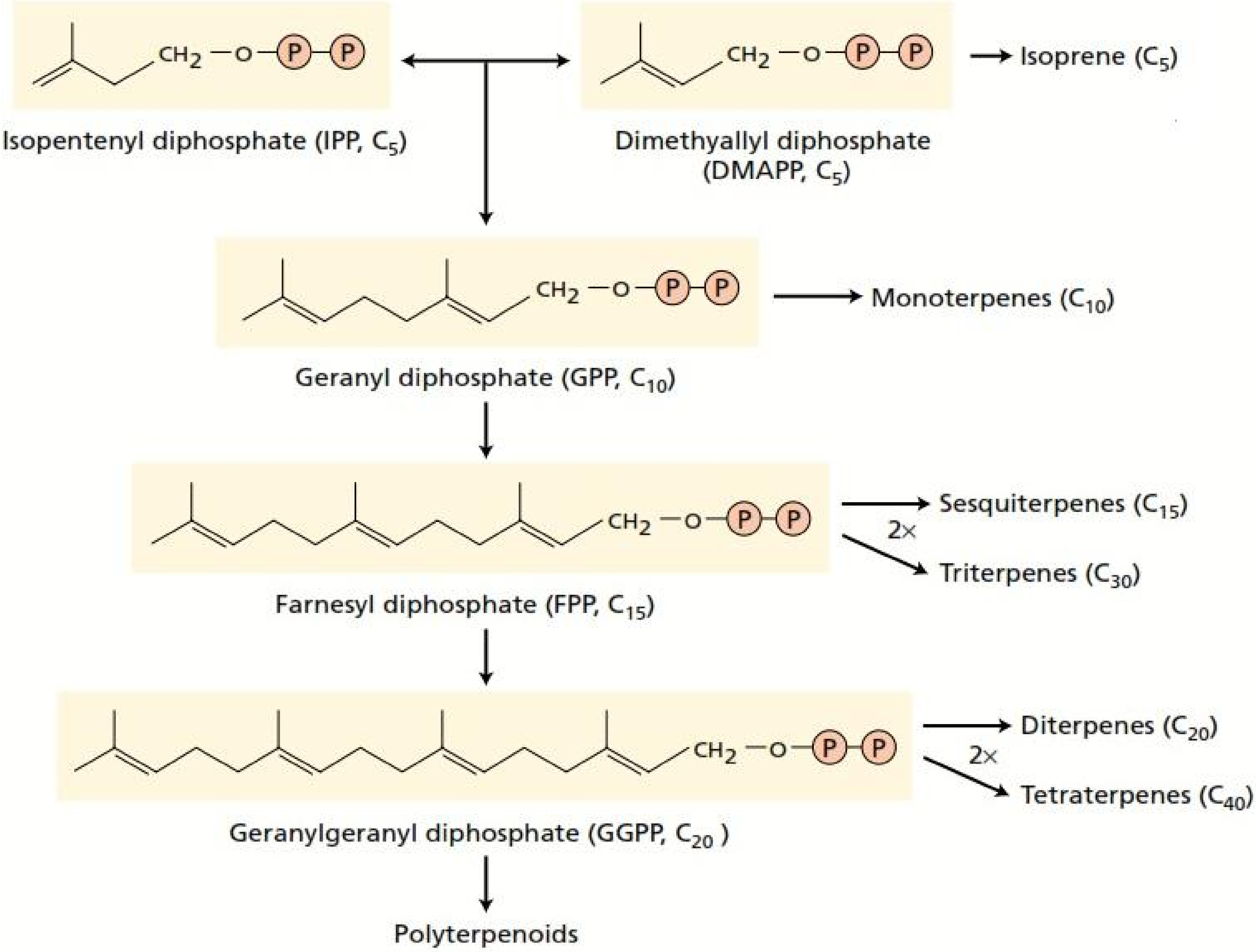
Phenylpropanoids

Benzenoids

MEP Pathway

- The MEP pathway involves seven enzymatic steps and begins with the condensation of D-glyceraldehyde 3-phosphate (**GAP**) and pyruvate (**Pyr**) to produce 1-deoxy-D-xylulose 5-phosphate (**DXP**), which is then subjected to isomerization with formation of the pathway's characteristic intermediate, **MEP**
- Five steps are required to convert MEP to **IPP** and **DMAPP (dimethyl allyl pyrophosphate)**


3× Acetyl-CoA (C_2)
Glyceraldehyde 3-phosphate (C_3)
Pyruvate (C_3)
Mevalonate pathway
Mevalonic acid
Methylerythritol phosphate (MEP)
Methylerythritol phosphate pathway
Isopentenyl diphosphate (IPP, C_5)
Dimethyallyl diphosphate (DMAPP, C_5)
Isoprene (C_5)



Isopentenyl diphosphate (IPP, C_5)

Dimethyallyl diphosphate (DMAPP, C_5)

→ Isoprene (C_5)

Geranyl diphosphate (GPP, C_{10})

→ Monoterpenes (C_{10})

Farnesyl diphosphate (FPP, C_{15})

→ Sesquiterpenes (C_{15})

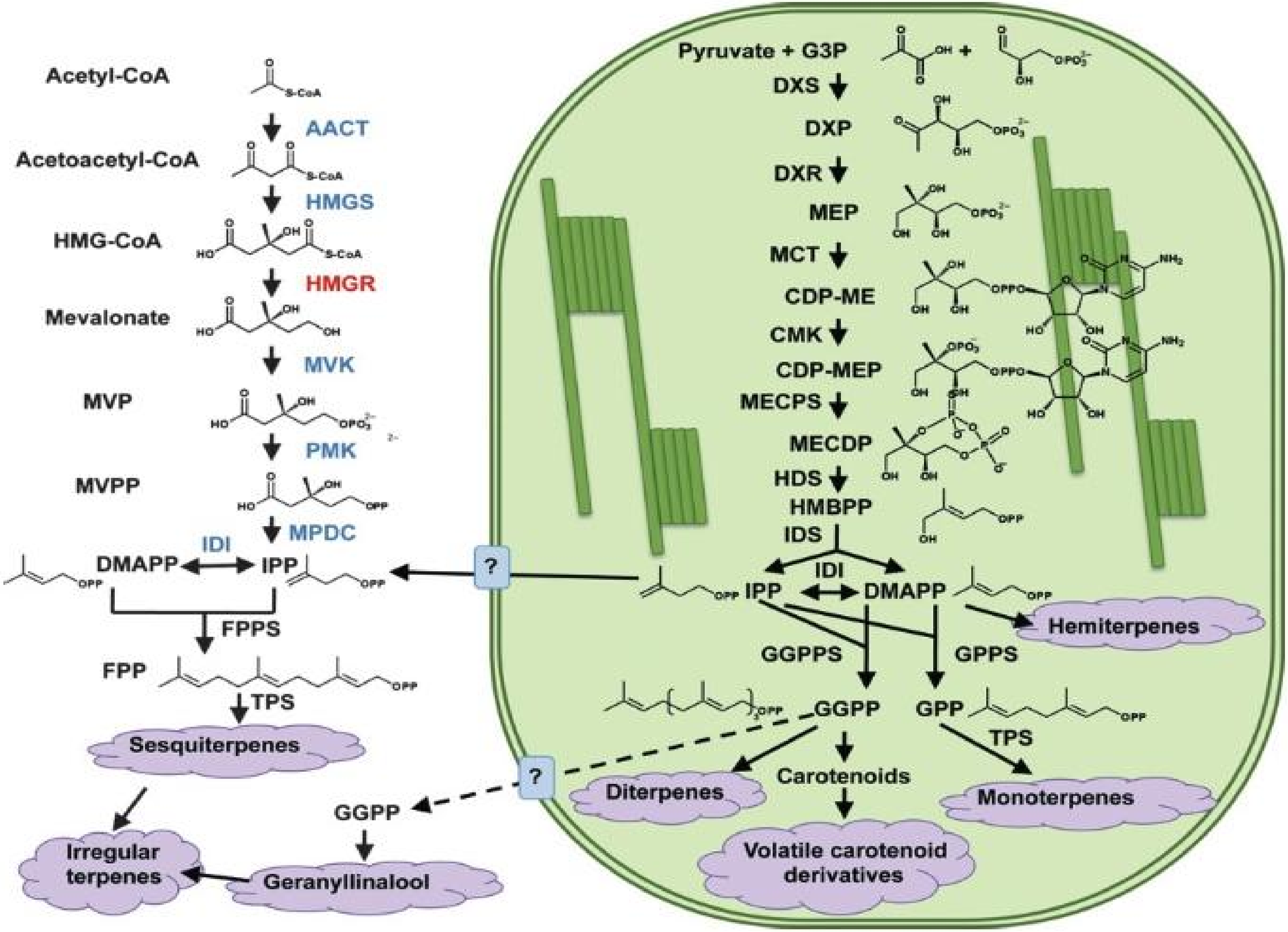
2× → Triterpenes (C_{30})

Geranylgeranyl diphosphate (GGPP, C_{20})

→ Diterpenes (C_{20})

2× → Tetraterpenes (C_{40})

Polyterpenoids



Acetyl-CoA

AACT

Acetoacetyl-CoA

HMGS

HMG-CoA

HMGR

Mevalonate

MVK

MVP

PMK

MVPP

MPDC

IDI

DMAPP

IPP

FPPS

FPP

TPS

Sesquiterpenes

Irregular terpenes

GGPP

Geranyllinalool

?

Pyruvate + G3P

DXS

DXP

DXR

MEP

MCT

CDP-ME

CMK

CDP-MEP

MECPS

MECDP

HDS

HMBPP

IDS

IPP

IDI

DMAPP

Hemiterpenes

GGPPS

GPPS

GGPP

GPP

TPS

Diterpenes

Carotenoids

Monoterpenes

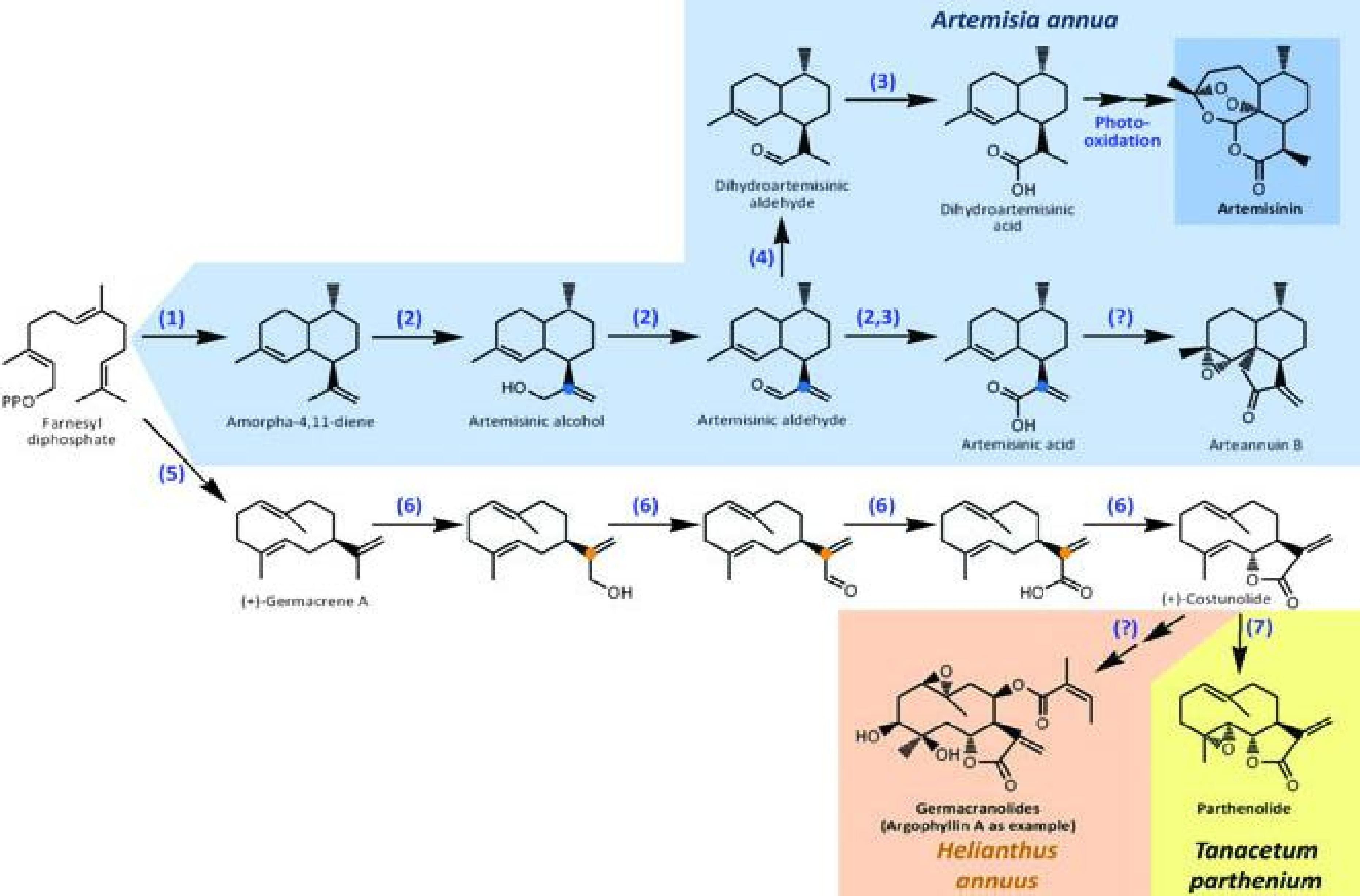
Volatile carotenoid derivatives

?

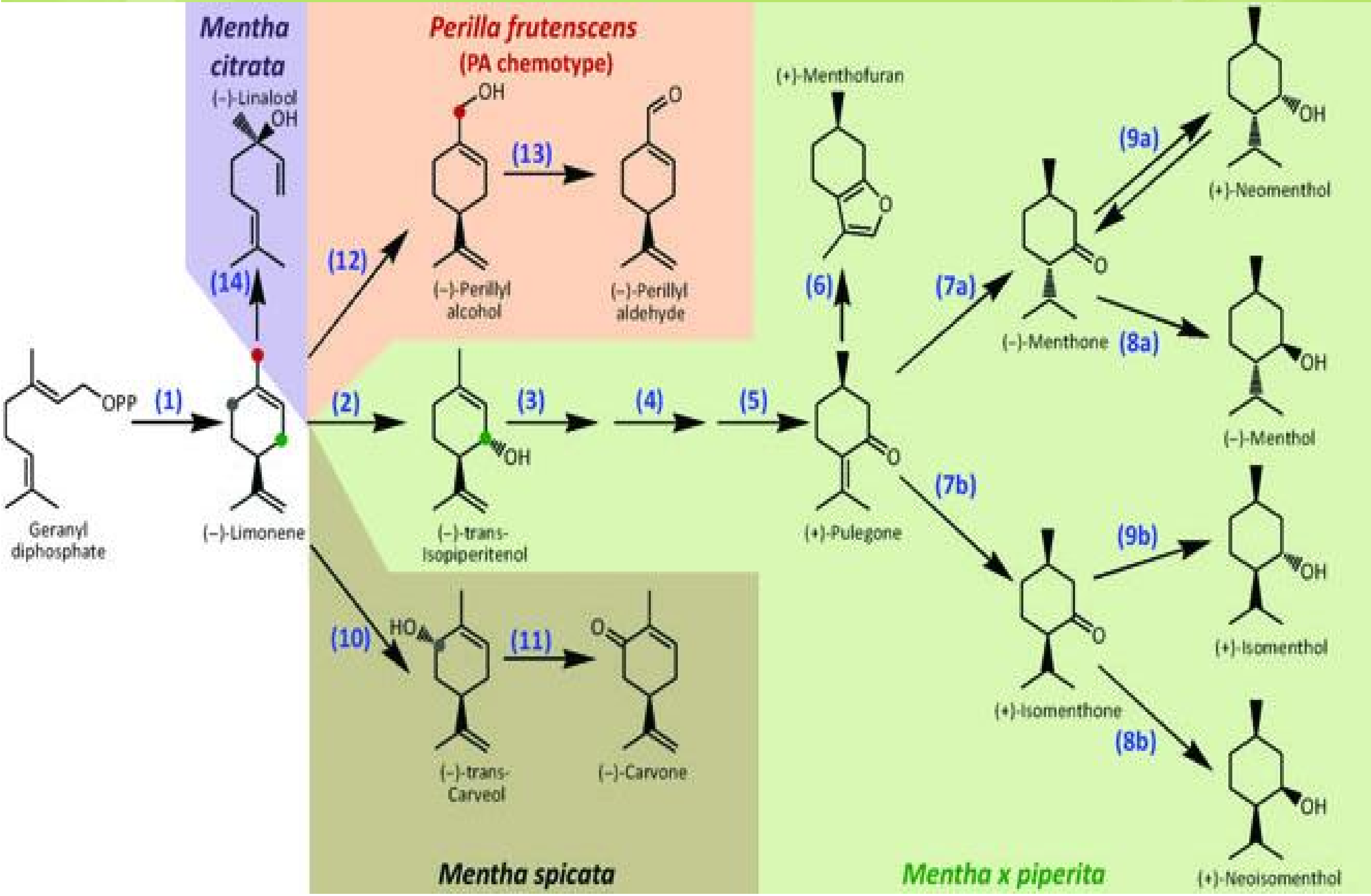
IPP and Its Isomer DMAPP

- **While the MVA pathway produces only IPP, the MEP pathway results in the synthesis of both IPP and DMAPP at a 6 : 1 ratio.**
- **Thus, both pathways rely on isopentenyl diphosphate isomerase (IDI), which reversibly converts IPP to DMAPP and controls the equilibrium between them.**
- **Recently, in *Catharanthus roseus* and *Arabidopsis thaliana* genomes, a single and two distinct IDI genes were identified, respectively**

Overview of sesquiterpene biosynthesis in Asteraceae

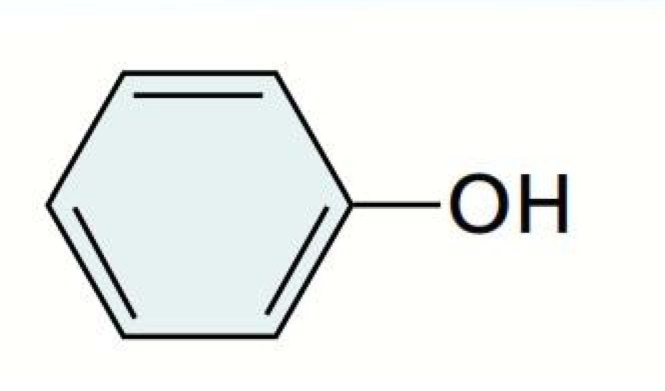


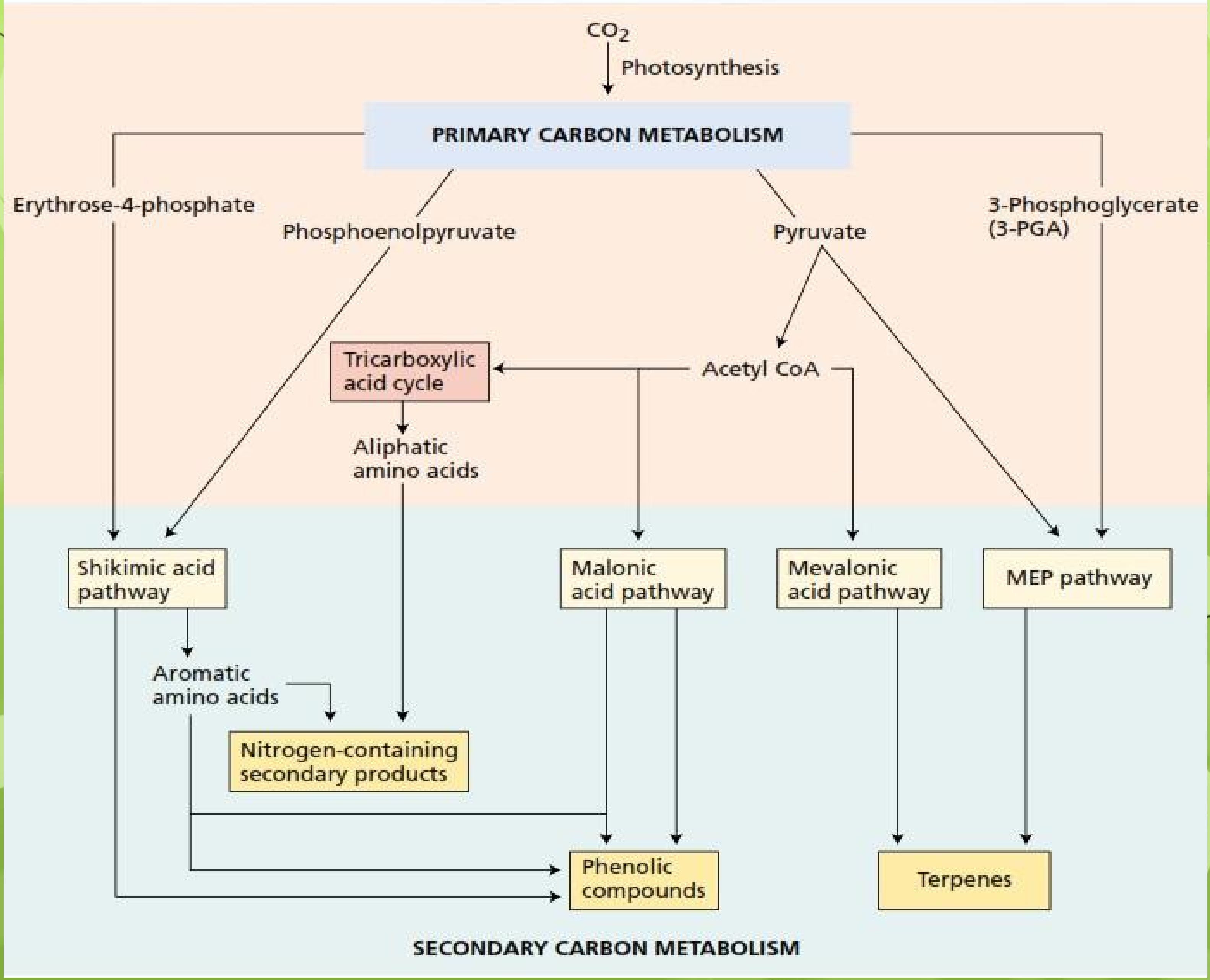
Overview of monoterpene biosynthesis in Lamiaceae



Phenolic compounds

- The second largest class of plant VOCs comprises phenylpropanoid and benzenoid compounds.
- Plants produce a large variety of secondary products that contain a phenol group—a hydroxyl functional group on an aromatic ring.





CO_2

Photosynthesis

PRIMARY CARBON METABOLISM

Erythrose-4-phosphate

Phosphoenolpyruvate

Pyruvate

3-Phosphoglycerate (3-PGA)

Tricarboxylic acid cycle

Acetyl CoA

Aliphatic amino acids

Shikimic acid pathway

Malonic acid pathway

Mevalonic acid pathway

MEP pathway

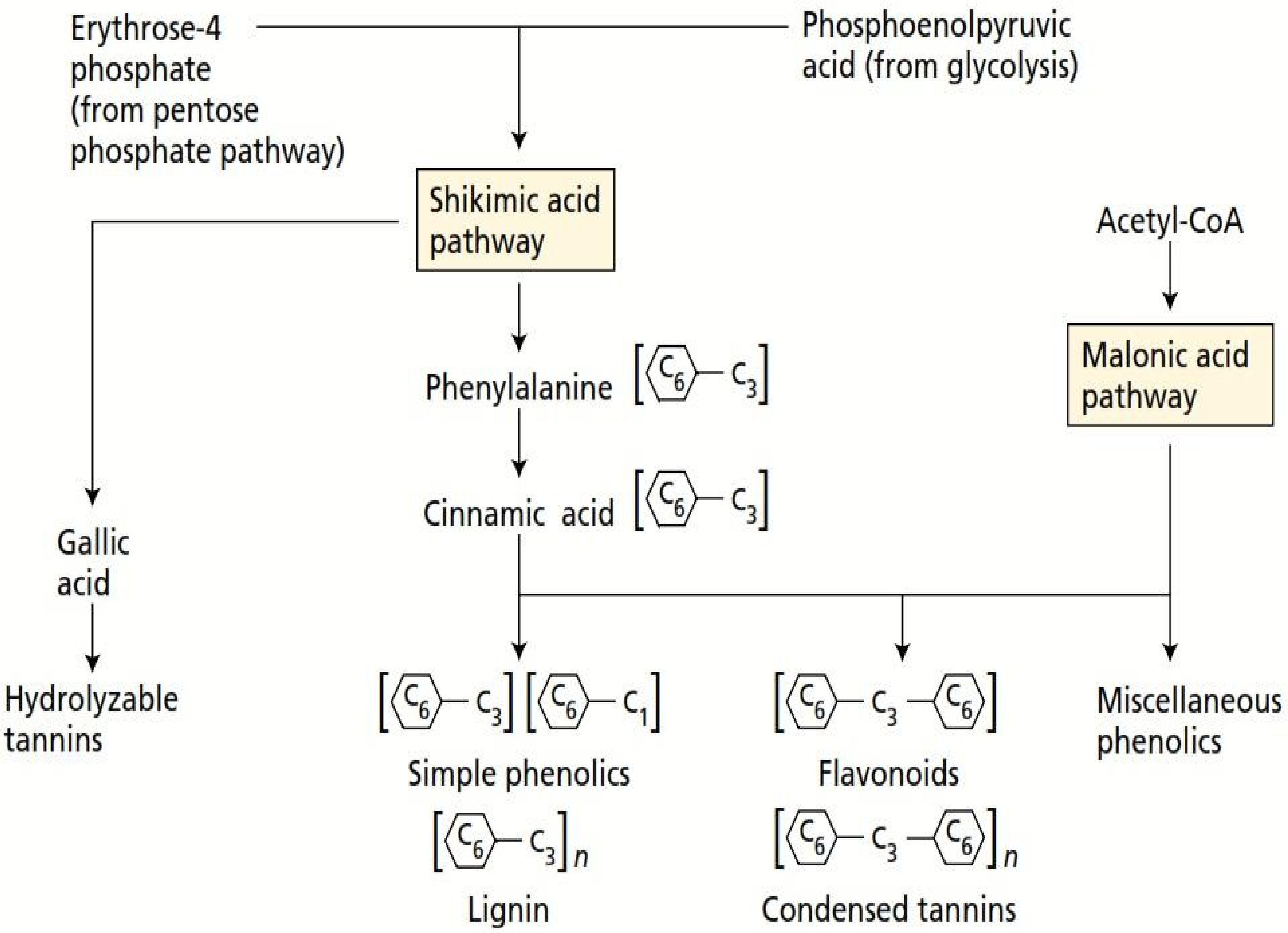
Aromatic amino acids

Nitrogen-containing secondary products

Phenolic compounds

Terpenes

SECONDARY CARBON METABOLISM



Erythrose-4 phosphate (from pentose phosphate pathway)

Phosphoenolpyruvic acid (from glycolysis)

Shikimic acid pathway

Acetyl-CoA

Malonic acid pathway

Phenylalanine $[C_6-C_3]$

Cinnamic acid $[C_6-C_3]$

Gallic acid

Hydrolyzable tannins

$[C_6-C_3]$ $[C_6-C_1]$

Simple phenolics

$[C_6-C_3]_n$

Lignin

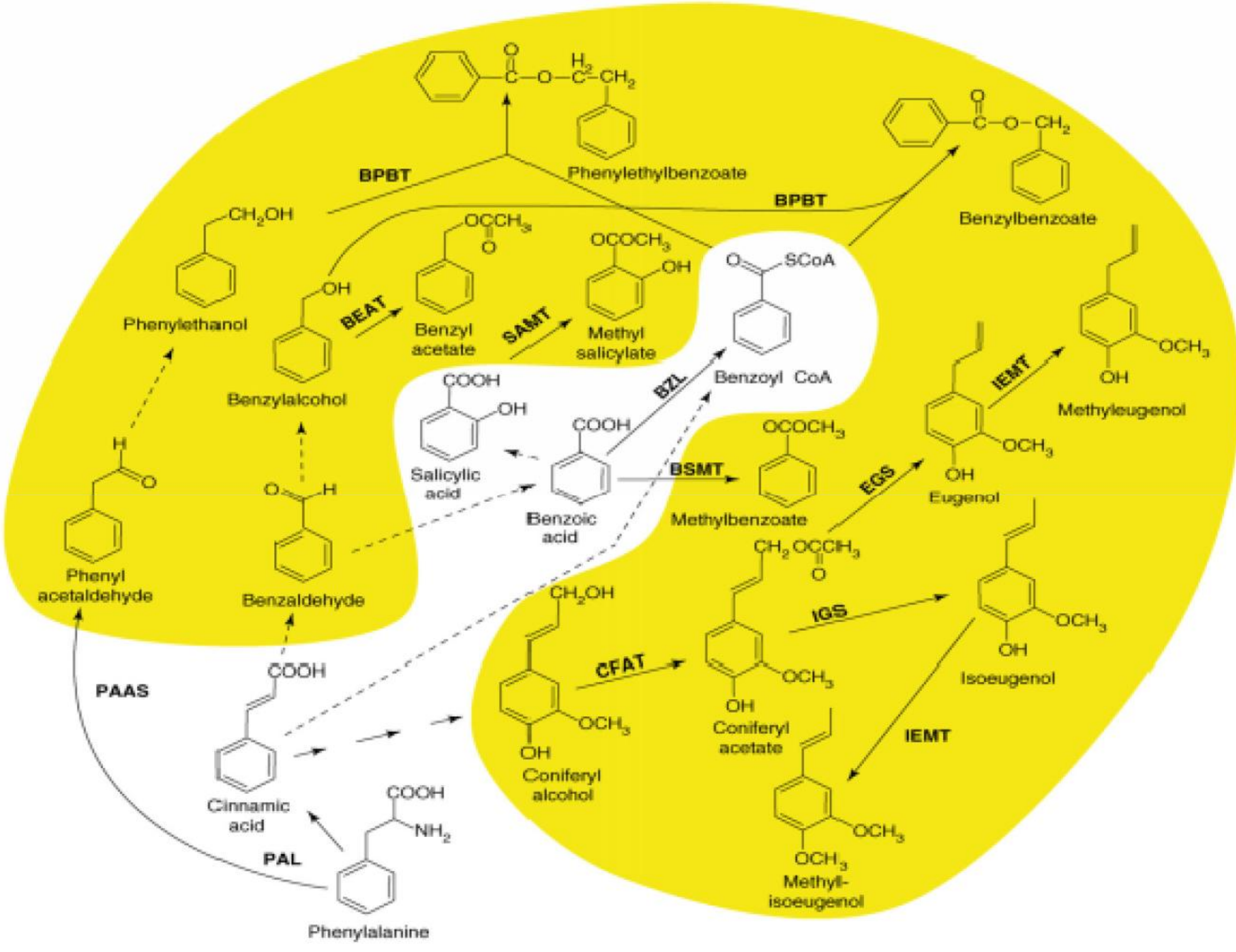
$[C_6-C_3-C_6]$

Flavonoids

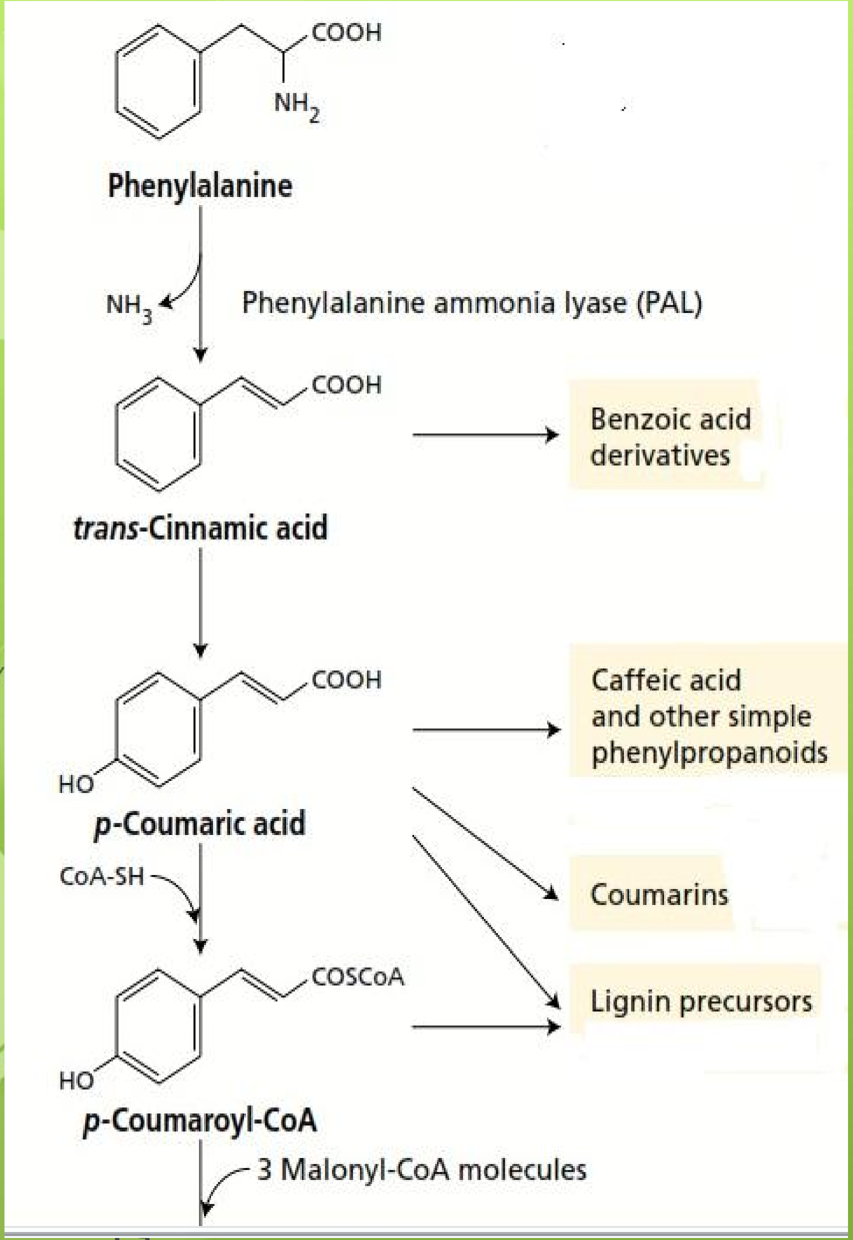
$[C_6-C_3-C_6]_n$

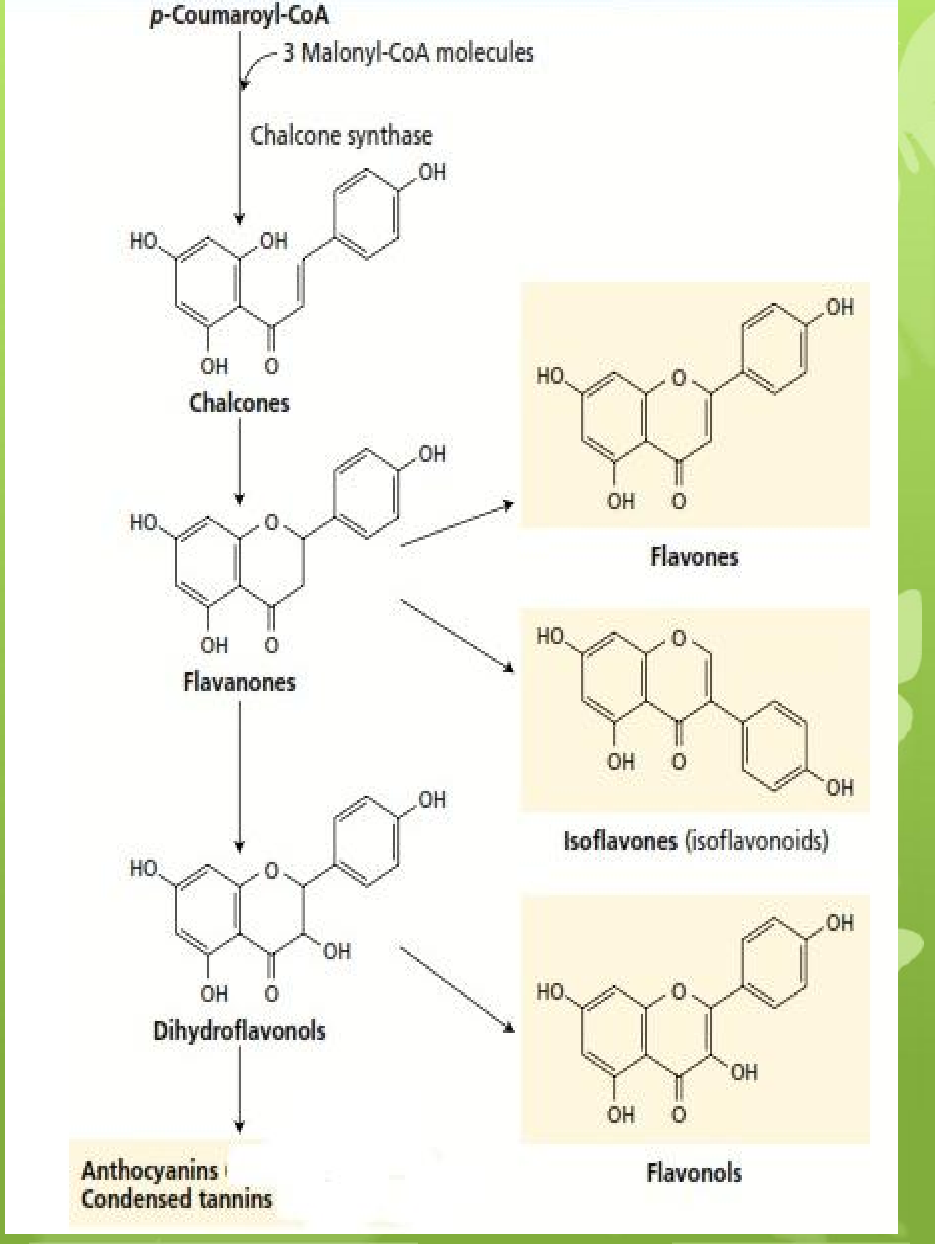
Condensed tannins

Miscellaneous phenolics

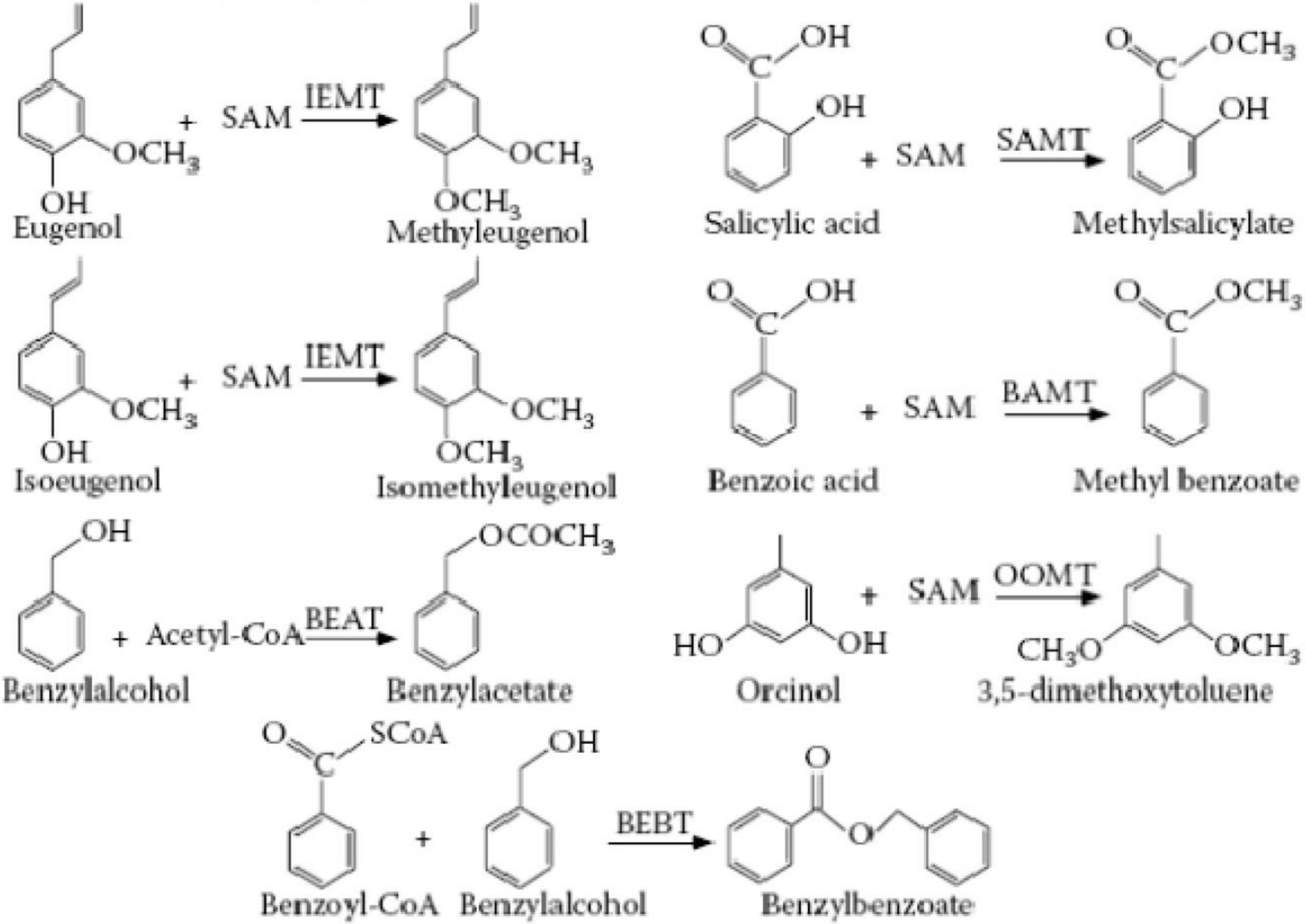


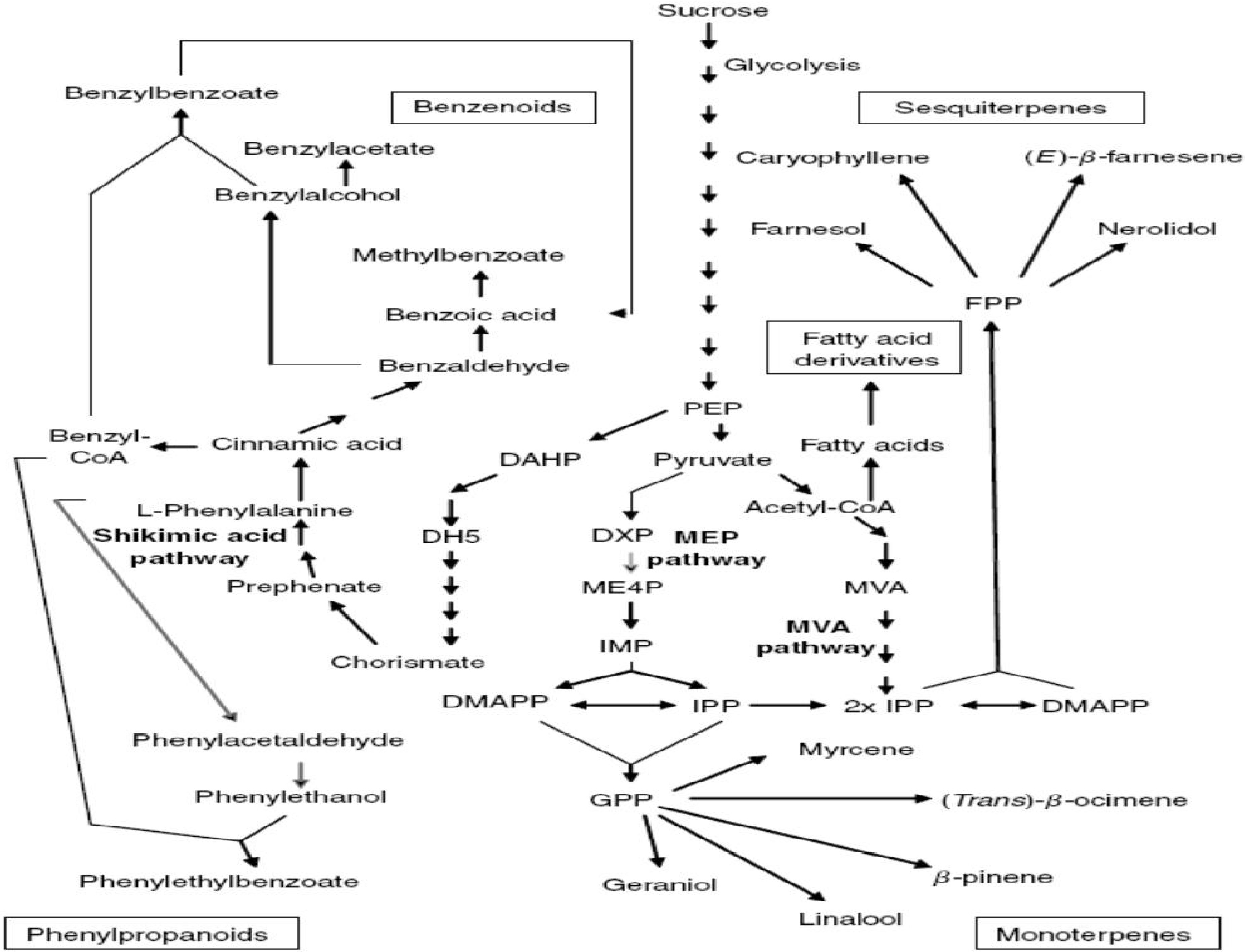
TRENDS in Biotechnology


COOH
NH2
Phenylalanine
NH3
Phenylalanine ammonia lyase (PAL)
COOH
trans-Cinnamic acid
Benzoic acid derivatives
COOH
HO
p-Coumaric acid
Caffeic acid and other simple phenylpropanoids
Coumarins
Lignin precursors
CoA-SH
COSCoA
HO
p-Coumaroyl-CoA
3 Malonyl-CoA molecules


p-Coumaroyl-CoA
3 Malonyl-CoA molecules
Chalcone synthase
HO
OH
OH
OH
O
Chalcones
Flavanones
Dihydroflavonols
Anthocyanins
Condensed tannins
Flavones
Isoflavones (isoflavonoids)
Flavonols

C. Benzenoids/phenylpropanoids





Sucrose

Glycolysis

Benzylbenzoate

Benzenoids

Sesquiterpenes

Benzylacetate

Caryophyllene

(*E*)-β-farnesene

Benzylalcohol

Farnesol

Nerolidol

Methylbenzoate

Benzoic acid

FPP

Fatty acid derivatives

Benzaldehyde

PEP

Benzyl-CoA

Cinnamic acid

DAHP

Pyruvate

Fatty acids

L-Phenylalanine

Acetyl-CoA

Shikimic acid pathway

DH5

DXP

MEP pathway

Prephenate

ME4P

MVA

MVA pathway

Chorismate

IMP

DMAPP

IPP

2x IPP

DMAPP

Phenylacetaldehyde

Myrcene

Phenylethanol

GPP

(*Trans*)-β-ocimene

Phenylethylbenzoate

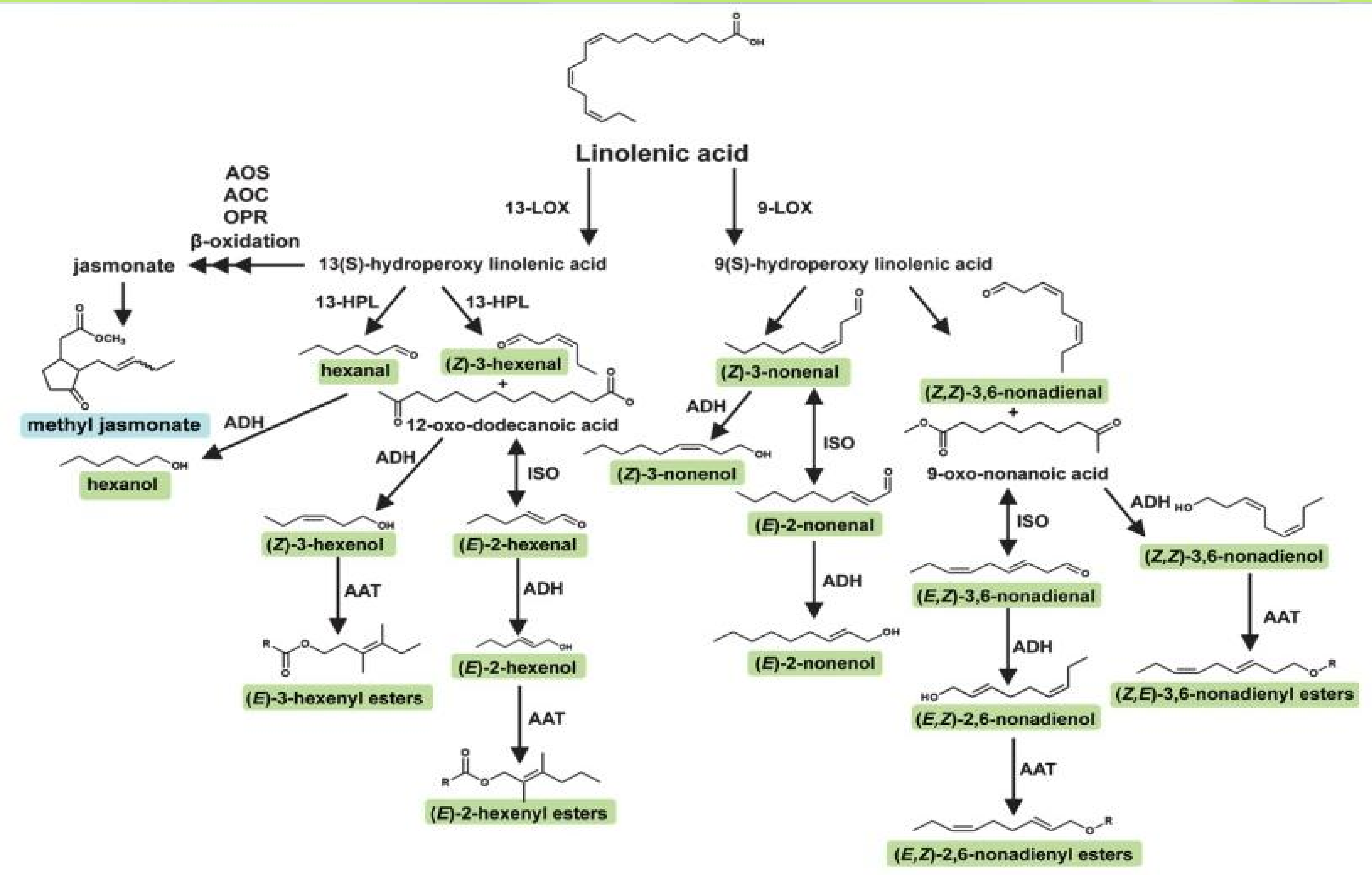
Geraniol

β-pinene

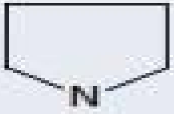
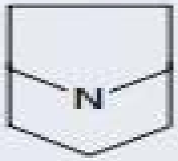
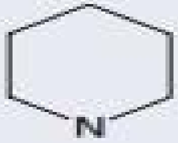
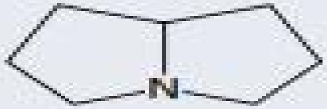
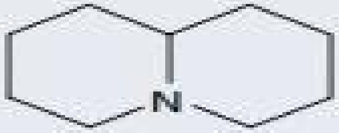
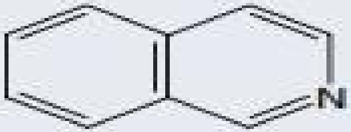
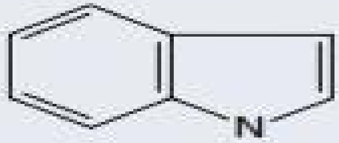
Linalool

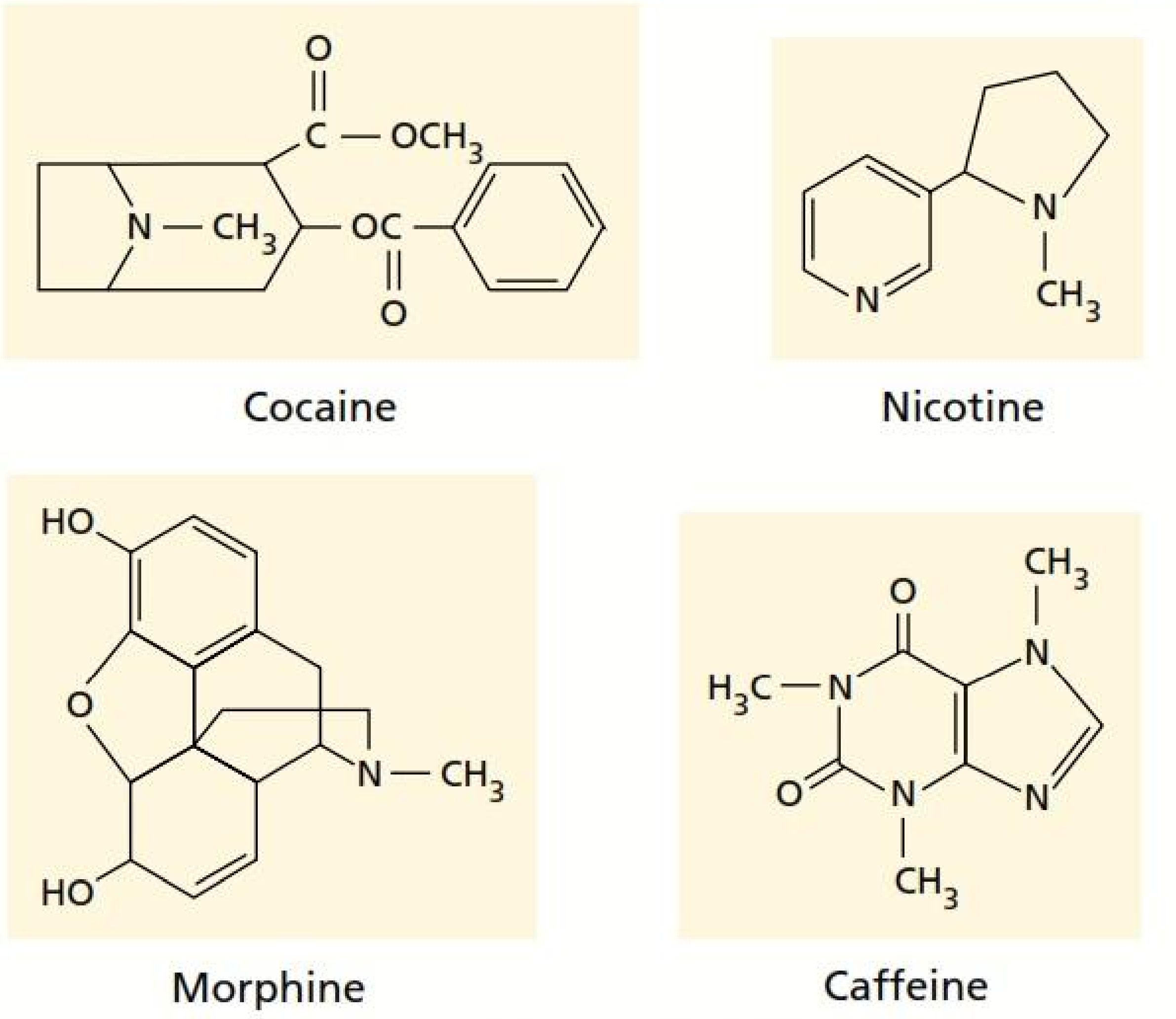
Phenylpropanoids

Monoterpenes



Synthesis of fatty acid-derived volatile organic compounds (VOCs) and green leaf volatiles (GLVs). Linoleic and linolenic acid serve as the precursors for a variety of fatty acid-derived VOCs. These precursors enter the lipoxygenase (LOX) pathway by an oxydation yielding 9-hydroperoxy and 13-hydroperoxy intermediates that are further converted to volatiles by hydroperoxide lyases and alcohol dehydrogenases. Stacked arrows illustrate the involvement of multiple enzymatic reactions. Volatile compounds are highlighted with a colored background, with green leaf volatiles shown in green. Abbreviations: AAT, alcohol acyltransferase; ADH, alcohol dehydrogenase; AOC, allene oxide cyclase; AOS, allene oxide synthase; 9-HPL, 9-hydroperoxide lyase; 13-HPL, 13- hydroperoxide lyase; ISO, isomerase; 9-LOX, 9-lipoxygenase; 13-LOX, 13-lipoxygenase; OPR, 12-oxophytodienoate reductase.

Alkaloid class	Structure	Biosynthetic precursor	Examples
Pyrrolidine		Ornithine (aspartate)	Nicotine
Tropane		Ornithine	Atropine Cocaine
Piperidine		Lysine (or acetate)	Coniine
Pyrrolizidine		Ornithine	Retrorsine
Quinolizidine		Lysine	Lupinine
Isoquinoline		Tyrosine	Codeine Morphine
Indole		Tryptophan	Psilocybin Reserpine Strychnine



Cocaine

Nicotine

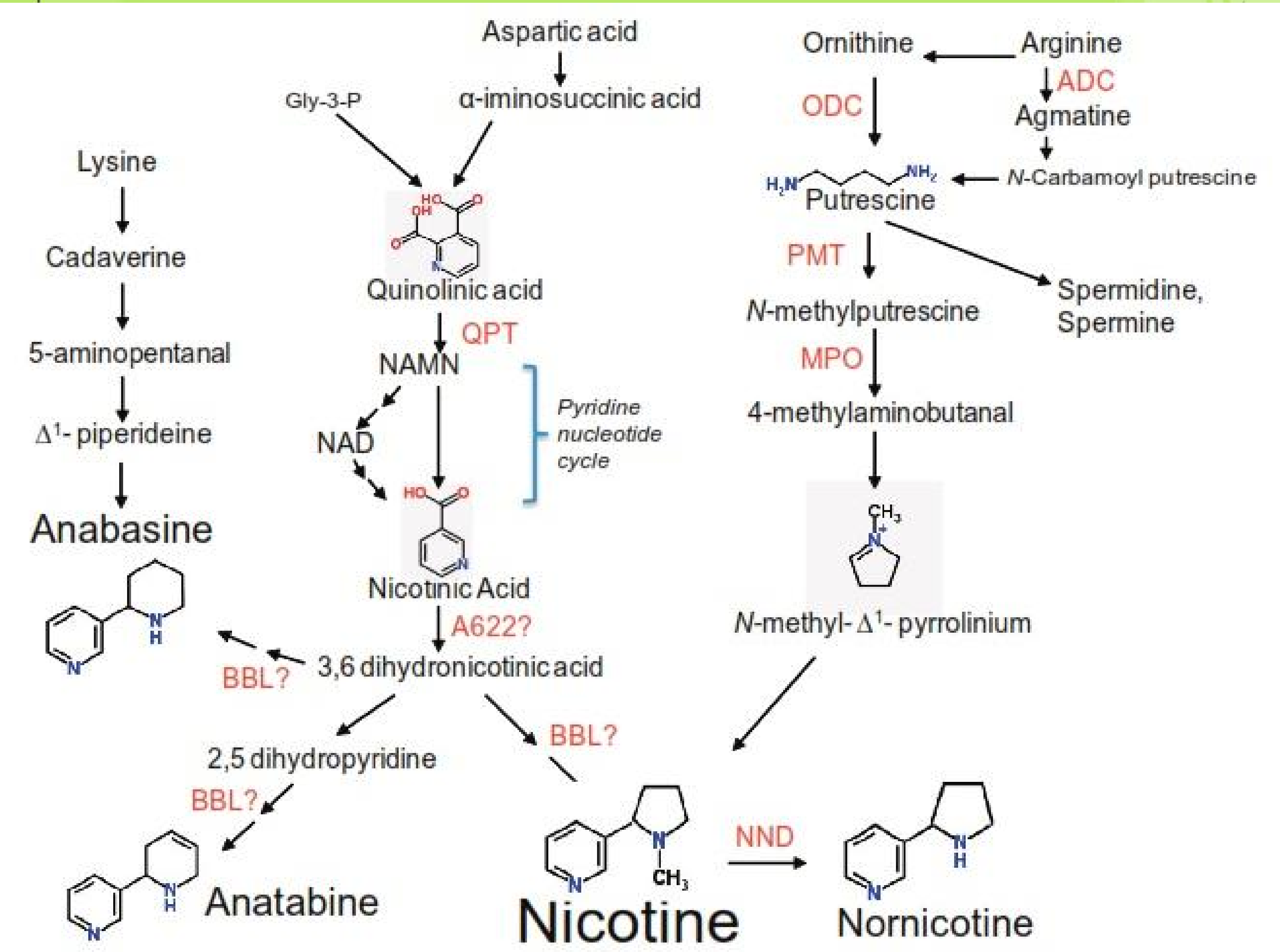
Morphine

Caffeine

Representative alkaloids

Examples of alkaloids, a diverse group of secondary metabolites that contain nitrogen, usually as part of a heterocyclic ring.

Caffeine is a purine-type alkaloid similar to the nucleic acid bases adenine and guanine. The pyrrolidine (five-membered) ring of nicotine arises from ornithine; the pyridine (six-membered) ring is derived from nicotinic acid.



Aspartic acid

Gly-3-P

α-iminosuccinic acid

Quinolinic acid

QPT

NAMN

NAD

Pyridine nucleotide cycle

Nicotinic Acid

A622?

3,6 dihydronicotinic acid

BBL?

2,5 dihydropyridine

BBL?

BBL?

Lysine

Cadaverine

5-aminopentanal

Δ¹- piperideine

Anabasine

Anatabine

Ornithine

Arginine

ADC

ODC

Agmatine

N-Carbamoyl putrescine

Putrescine

PMT

Spermidine, Spermine

N-methylputrescine

MPO

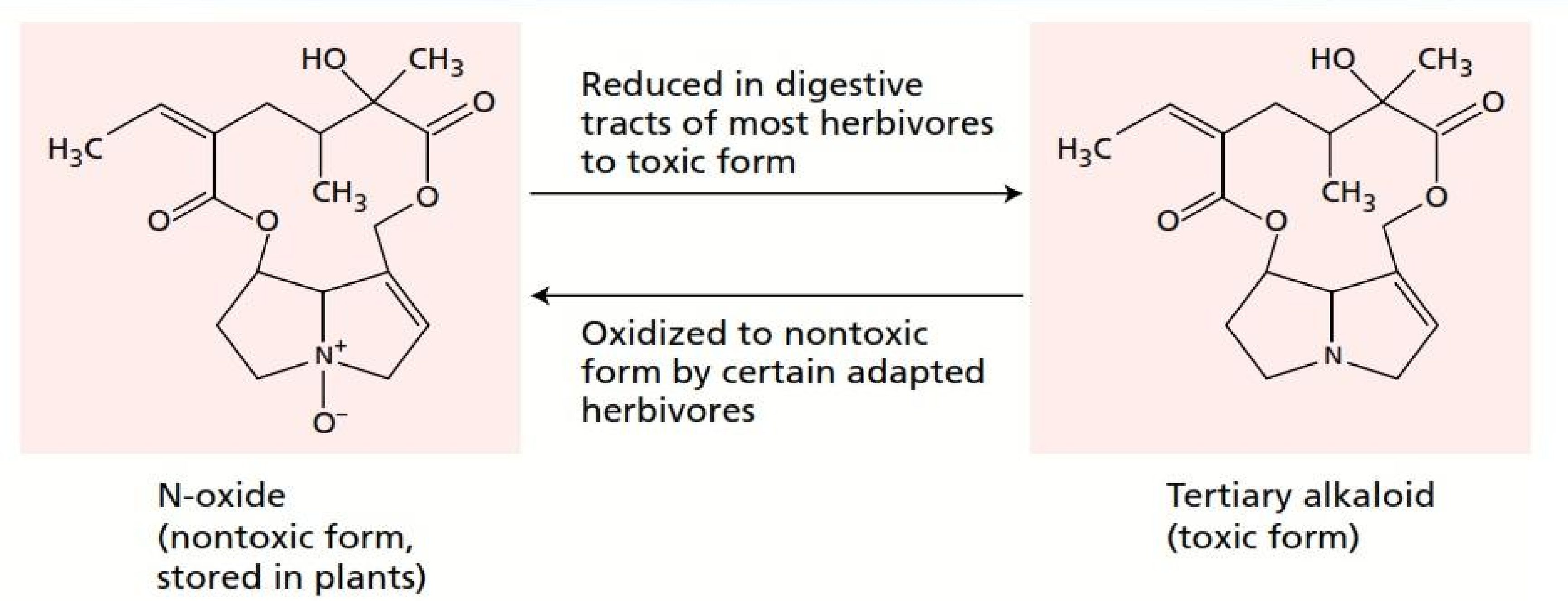
4-methylaminobutanal

N-methyl- Δ¹- pyrrolinium

Nicotine

NND

Nornicotine



Reduced in digestive tracts of most herbivores to toxic form

Oxidized to nontoxic form by certain adapted herbivores

N-oxide (nontoxic form, stored in plants)

Tertiary alkaloid (toxic form)

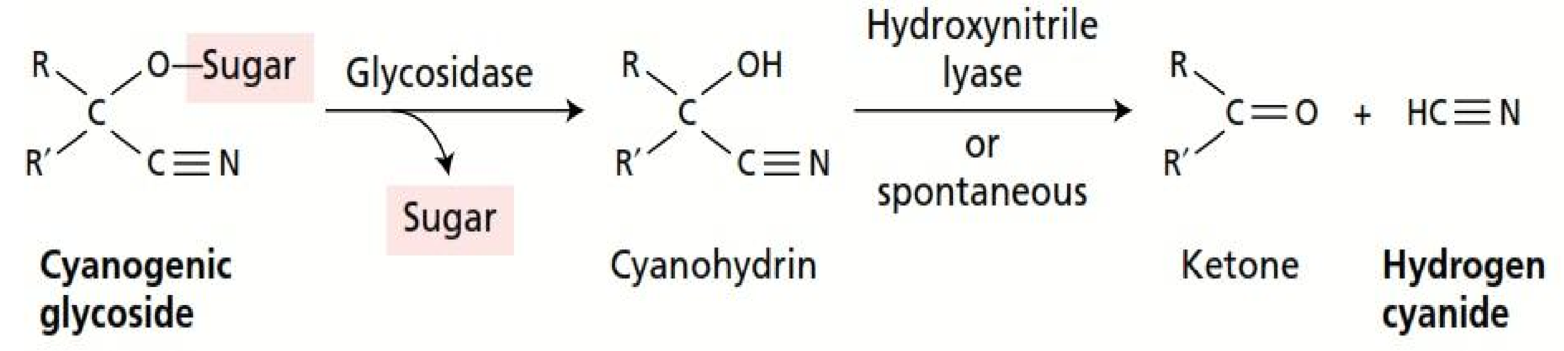
Two forms of pyrrolizidine alkaloids occur in nature: the N-oxide form and the tertiary alkaloid.

The nontoxic N-oxide found in plants is reduced to the toxic tertiary form in the digestive tracts of most herbivores.

However, some adapted herbivores can convert the toxic tertiary alkaloid back to the nontoxic N- oxide.

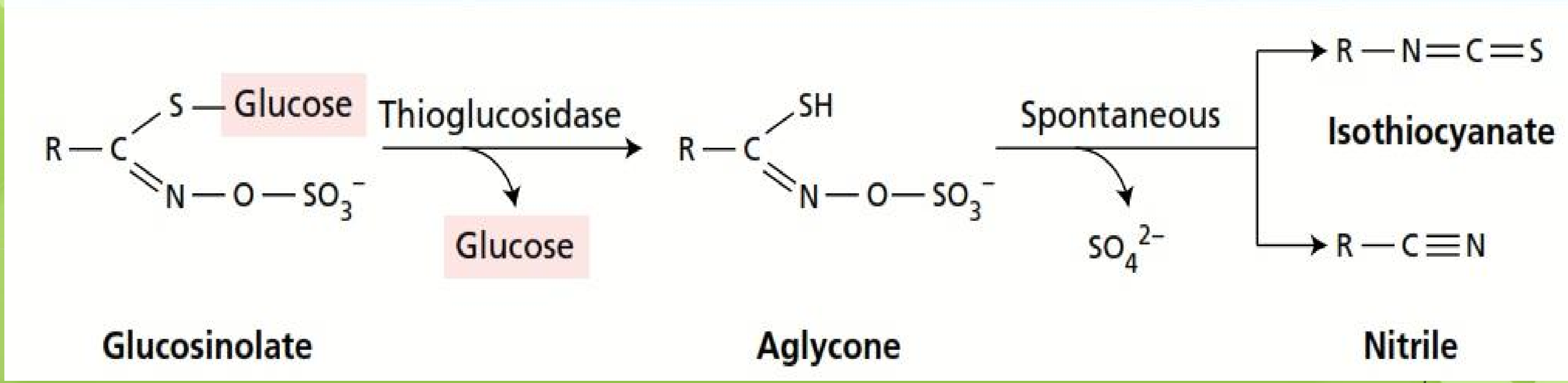
These forms are illustrated here for the alkaloid senecionine, found in species of *Senecio*.

Cyanogenic Glycosides

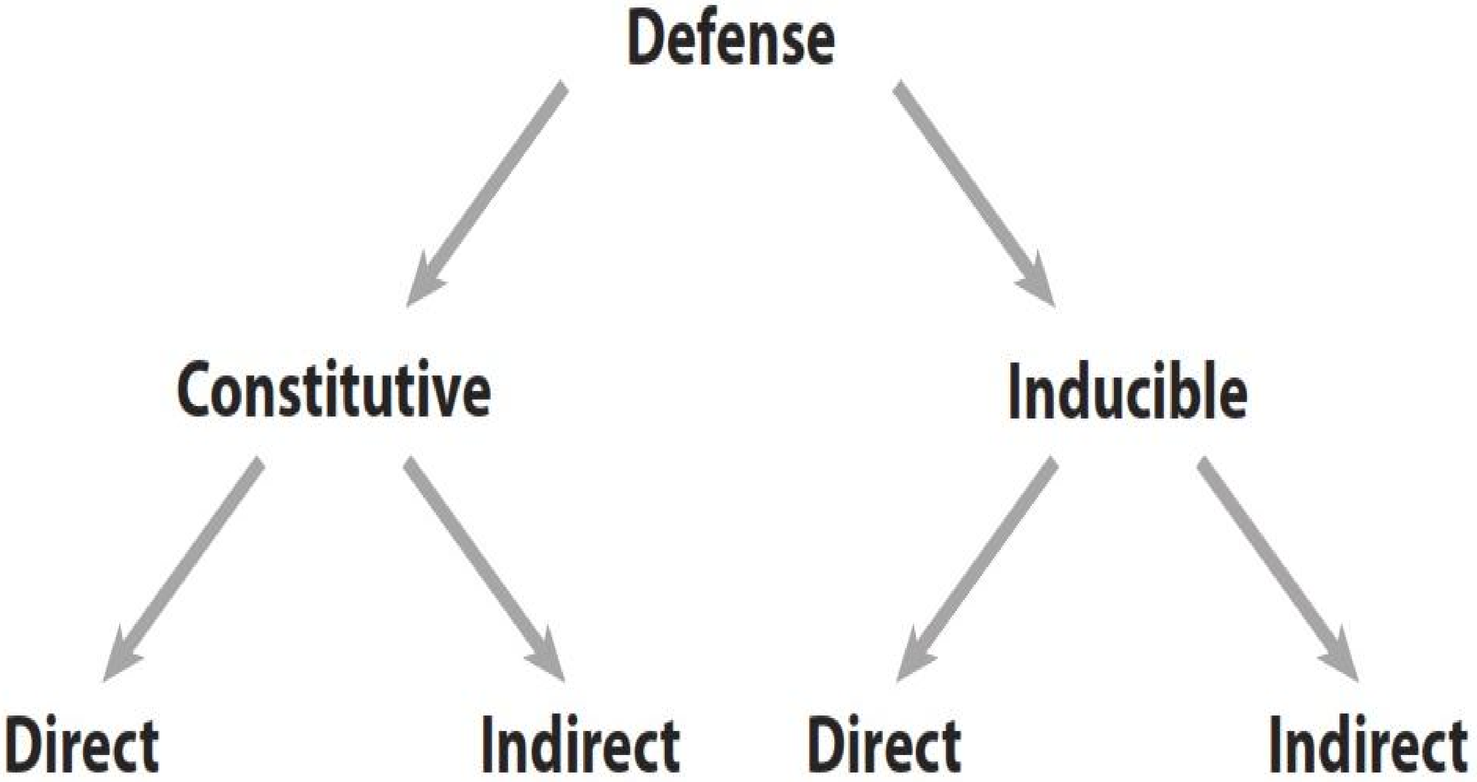


The breakdown of cyanogenic glycosides in plants is a two-step enzymatic process.

Glucosinolate



Hydrolysis of glucosinolates to mustard-smelling volatiles.



Defense

Constitutive

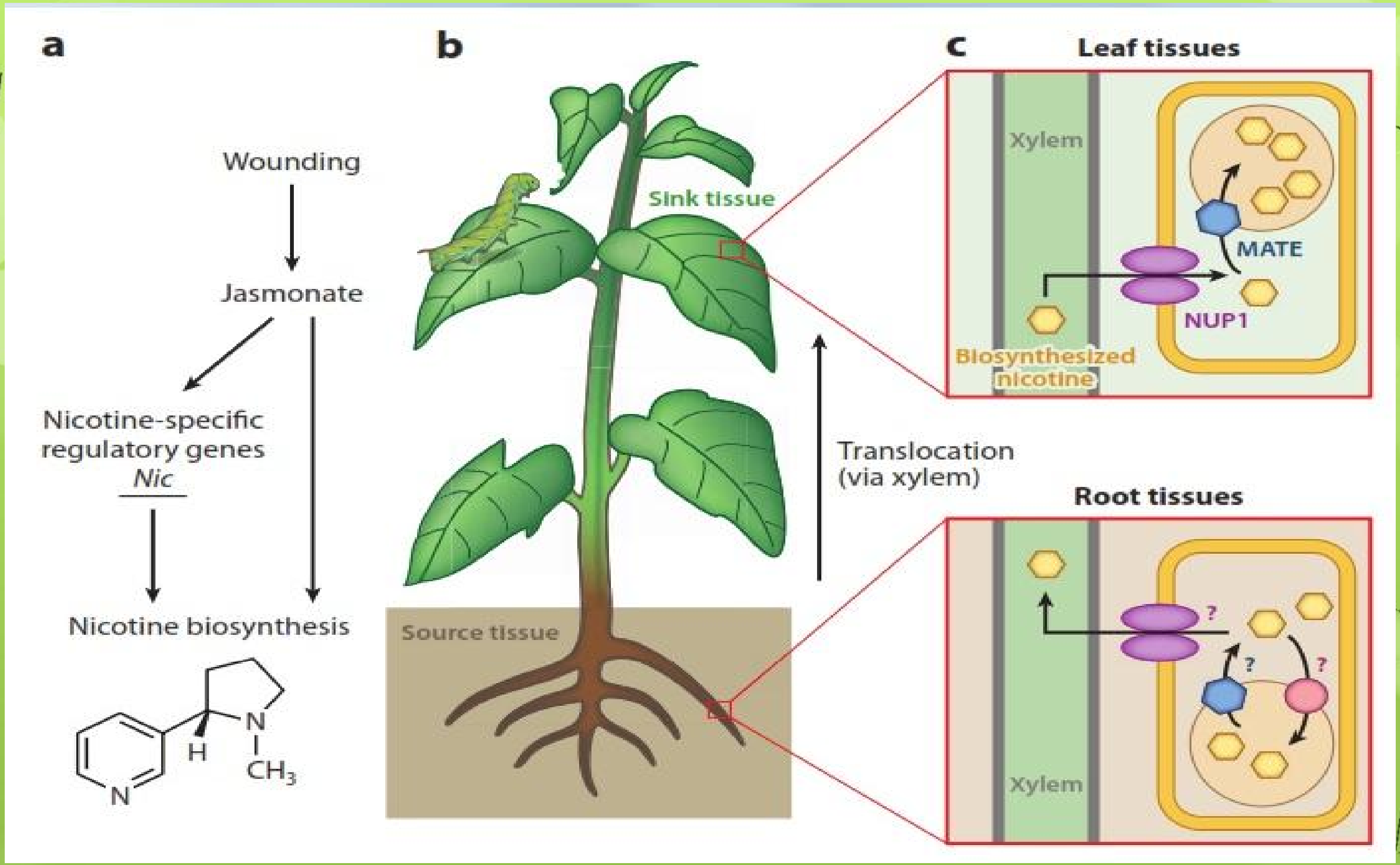
Inducible

Direct

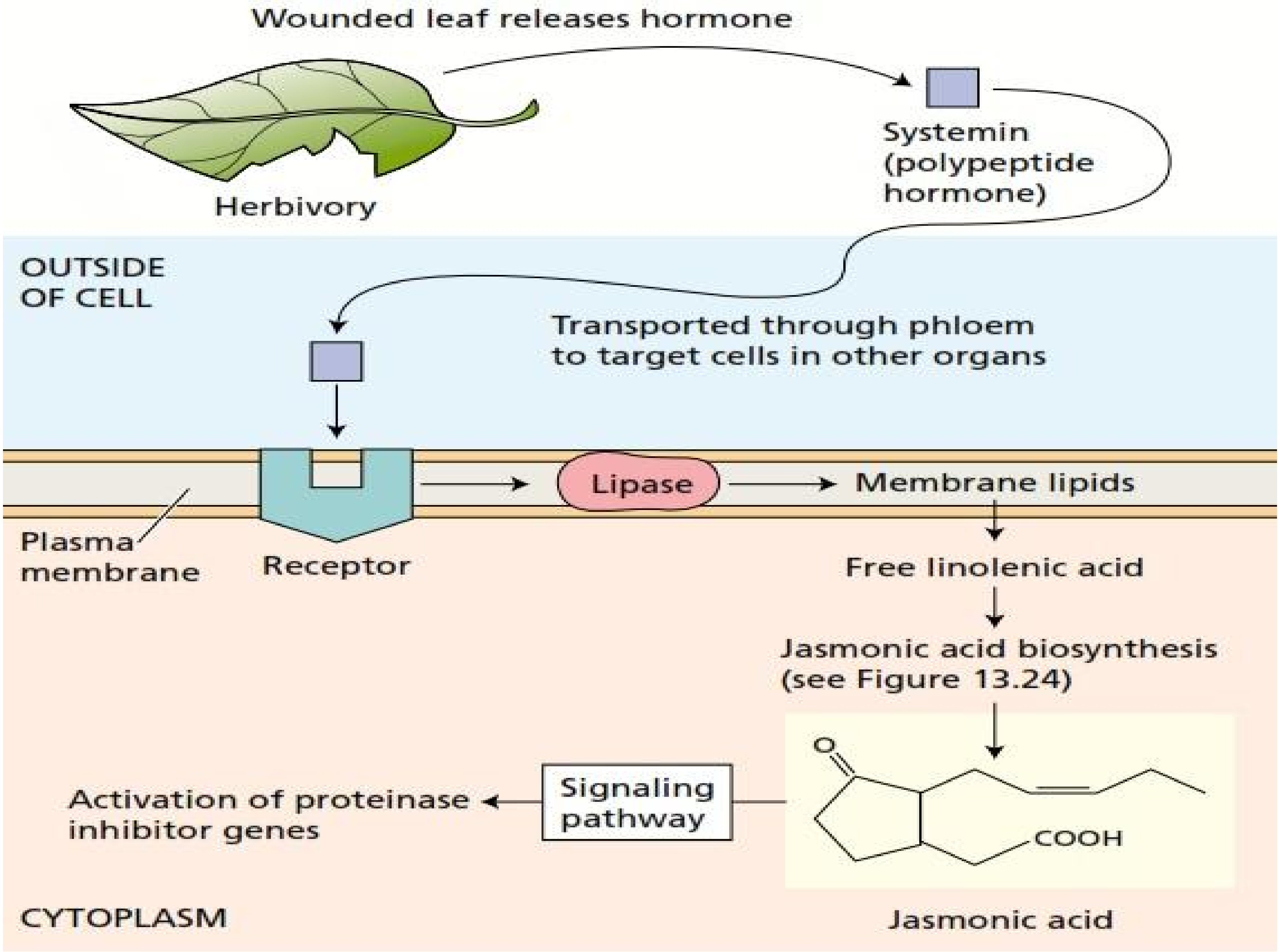
Indirect

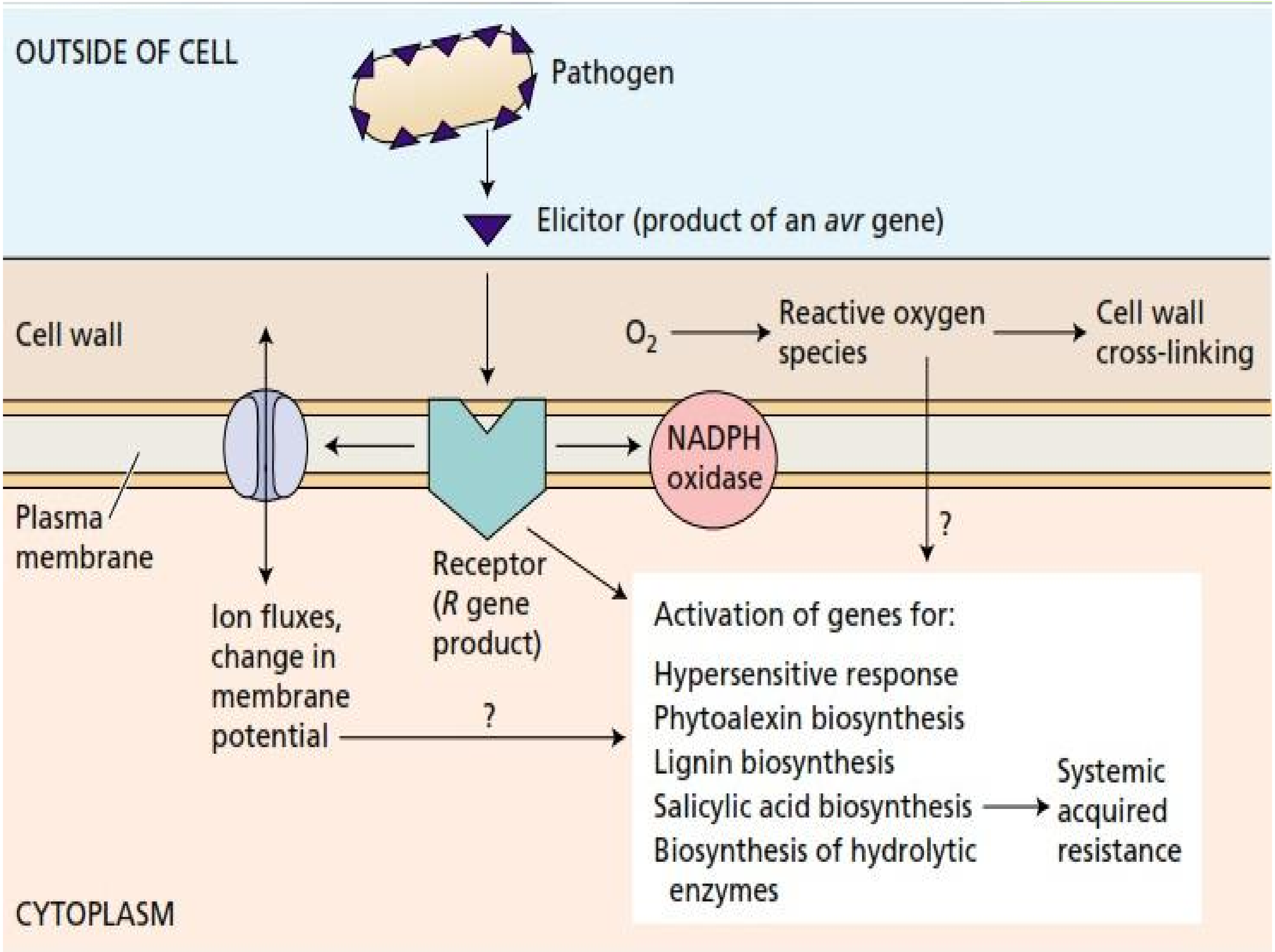
Direct

Indirect



Model for herbivore/wounding-mediated nicotine accumulation in the leaves of *Nicotiana tabacum*.
(a) The herbivory-induced phytohormone jasmonate is transported by the phloem to the roots and triggers nicotine biosynthesis along with upregulation of the required transporters.
(b) Illustration of the transport routes with transporters in tobacco plants.
(c) The biosynthesized nicotine (yellow hexagons) is loaded via a jasmonic acid–induced multidrug and toxic compound extrusion (MATE) transporter into the vacuole.
In the leaves a second transporter, nicotine uptake permease (NUP1), translocates the alkaloid from the xylem to the leaf cells. The three different transporters in the roots are still not identified, as indicated by the question marks.


Wounded leaf releases hormone
Herbivory
Systemin (polypeptide hormone)
OUTSIDE OF CELL
Transported through phloem to target cells in other organs
Lipase
Membrane lipids
Plasma membrane
Receptor
Free linolenic acid
Jasmonic acid biosynthesis (see Figure 13.24)
O
COOH
Activation of proteinase inhibitor genes
Signaling pathway
CYTOPLASM
Jasmonic acid



OUTSIDE OF CELL

Pathogen

Elicitor (product of an *avr* gene)

Cell wall

O_2 → Reactive oxygen species → Cell wall cross-linking

Plasma membrane

NADPH oxidase

Receptor (*R* gene product)

Ion fluxes, change in membrane potential

?

?

Activation of genes for:

Hypersensitive response

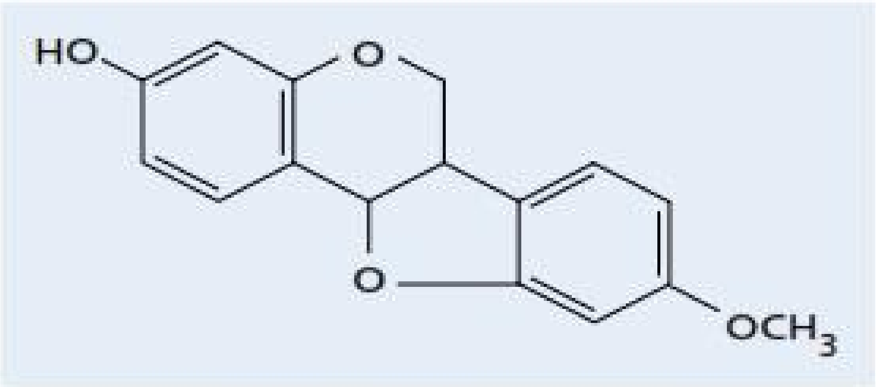
Phytoalexin biosynthesis

Lignin biosynthesis

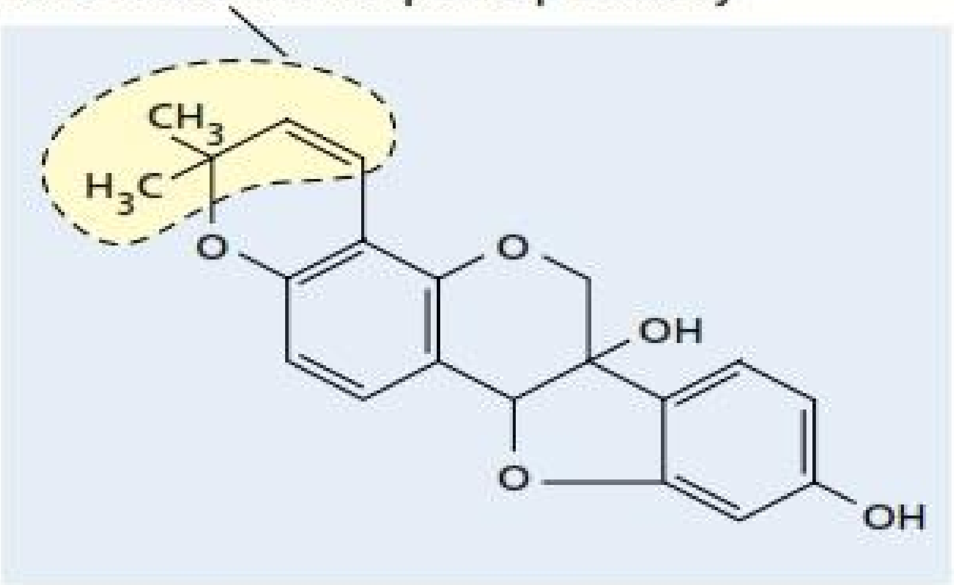
Salicylic acid biosynthesis → Systemic acquired resistance

Biosynthesis of hydrolytic enzymes

CYTOPLASM



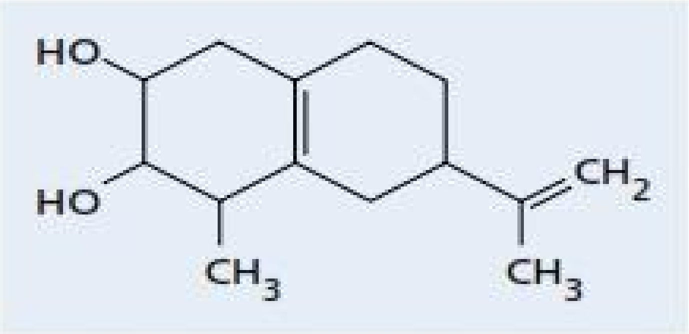
Medicarpin (from alfalfa)



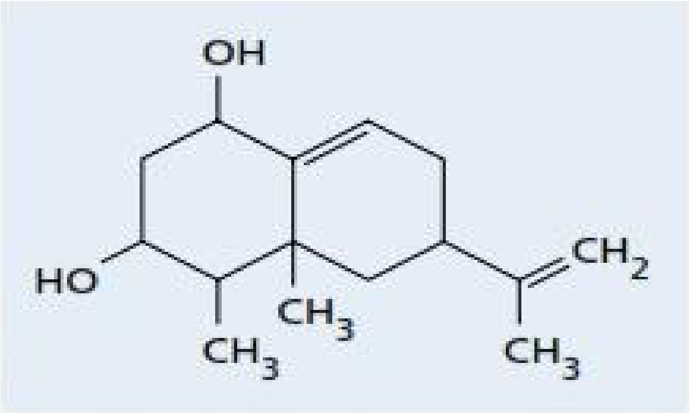
Additional ring formed from a C_5 unit from the terpene pathway

Glyceollin I (from soybean)

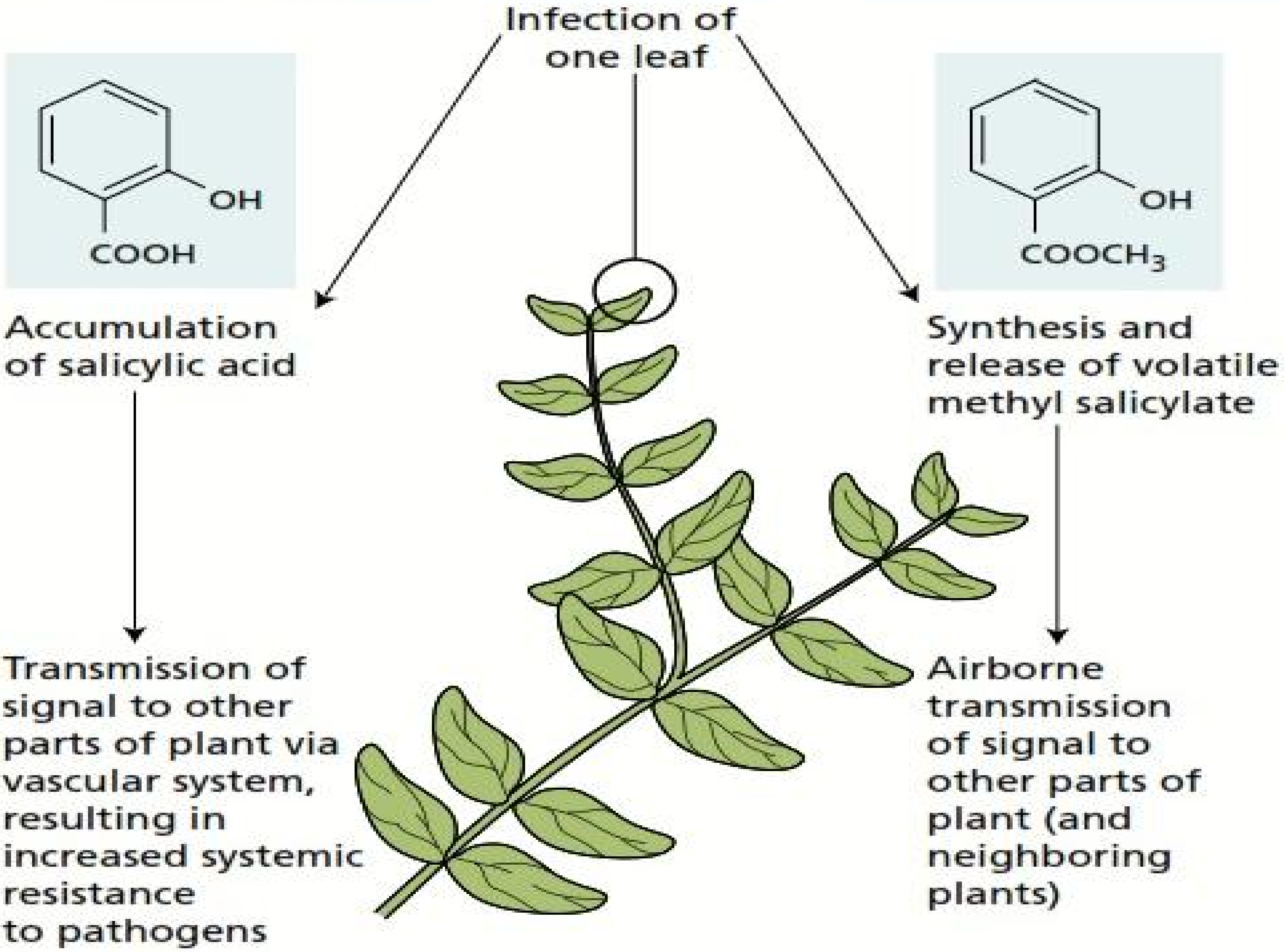
Isoflavonoids from the Leguminosae (the pea family)



Rishitin (from potato and tomato)



Capsidiol (from pepper and tobacco)



Infection of one leaf

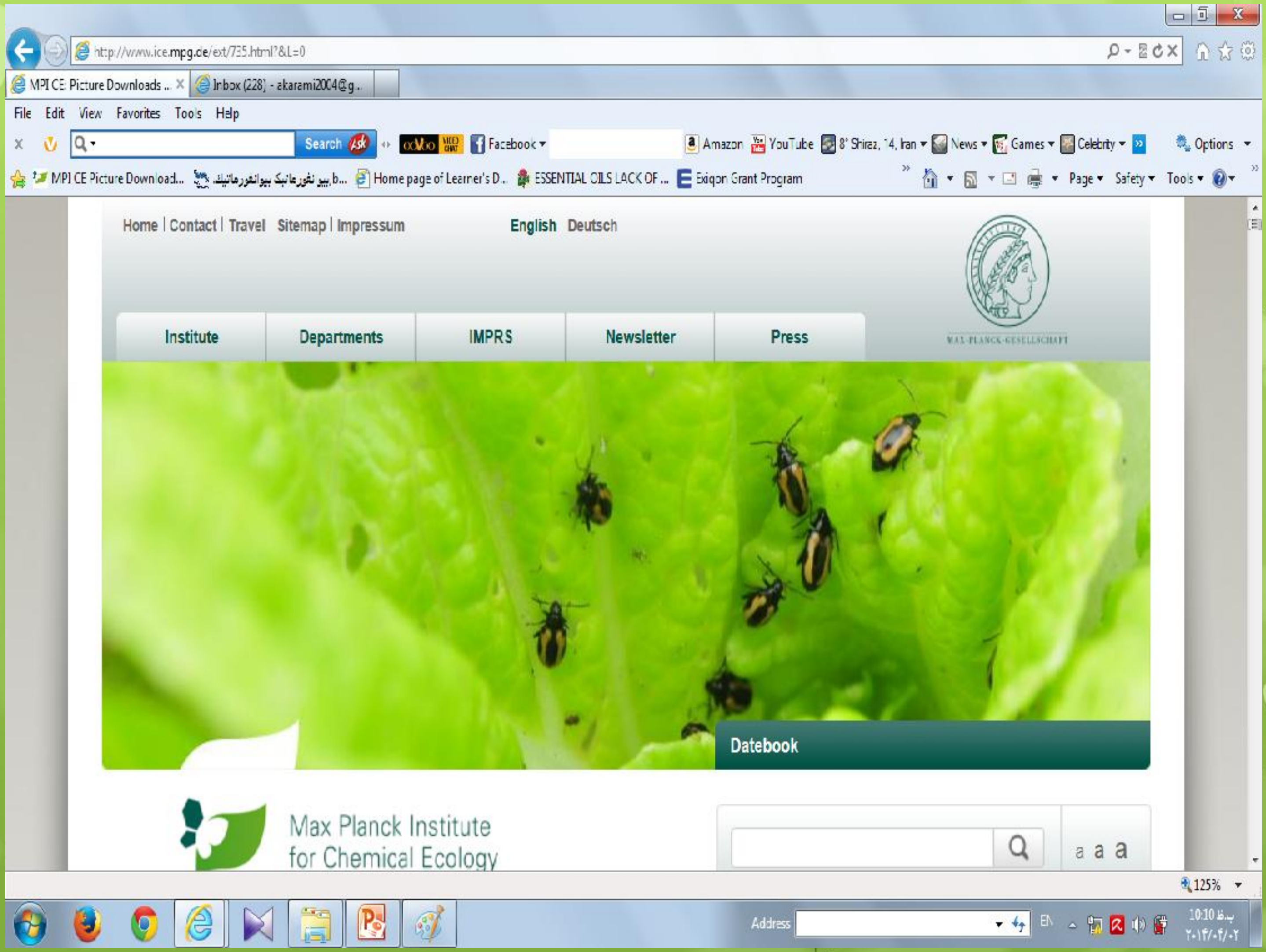
Accumulation of salicylic acid

Transmission of signal to other parts of plant via vascular system, resulting in increased systemic resistance to pathogens

Synthesis and release of volatile methyl salicylate

Airborne transmission of signal to other parts of plant (and neighboring plants)

http://www.ice.mpg.de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